Generation of elusive neutrals and dications by neutralization resp. Charge stripping of monocations in beam experiments

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Abstract - The diluted gas phase within a mass spectrometer is
ideally suited for performing collision experiments of fast
moving ions with thermalized target atoms. Among the many re-
actions which can be brought about with a given cation are its
selective reduction, i. e. neutralization, or the oxidation
to generate multiply-charged cations. These experiments allow
the "tailored synthesis" of a variety of unusual chemical spe-
cies, which because of intermolecular processes cannot be pre-
pared or studied in solution or in a matrix. Among the neutral
molecules which have been generated in our laboratory in this
way and which are discussed in this contribution are mono-
and disubstituted acetylenes XC≡CY (X = H, Y = OH, NH_2; X = Y
= OH, NH_2), the long-sought after carbonic (H_2CO_3), carbamic
(HOC(O)NH_2) and sulfurous acid (H_2SO_3), the dimer of CS, i. e.
ethylenedithione (CS)$_2$, and elusive organometallic neutral
fragments like FeCH$_x$ (x = 0 - 3) or MC$_5$H$_5$ (M = Fe, Co, Ni).
Charge stripping experiments constitute an extremely conven-
ient way to generate small organic dications in the gas phase.
Some of the remarkable properties of these species, which in
spite of substantial electrostatic repulsion ("coulomb explo-
sion") are very often metastable, are indicated by high level
ab initio MO calculations and confirmed by beam experiments
using tandem mass spectrometry.

INTRODUCTION

Quite a few molecular species can only be generated in the gas phase because
in solution or even in the solid state intermolecular interactions will make
them unstable and lead to isomerization, polymerization or dissociation (ref.
1 - 3). The diluted gas phase which exists in a mass spectrometer is ideally
suited for the study of isolated molecules. First of all, as the experiments
are conducted in the absence of any counterions and solvents one does not
have to account for any possible intermolecular effects. Secondly, the past
ten years have witnessed an impressive development in mass spectrometric
methodologies (ref. 4 - 8) for the tailor-made generation and characteriza-
tion of solitary ions with unusual structures and/or intriguing properties.
Among the species studied are not only singly-charged ions, but also di- and
polycations, which are produced from a high kinetic energy beam of mono-cat-
ions via charge-stripping mass spectrometry (CSMS) (ref. 9 - 10), as well as

unique neutrals. The latter can easily be generated and characterized by the promising technique of neutralization/reionization mass spectrometry (NRMS) (ref. 13 - 15). Without going into technical details, the experiments consist of the following steps:

<u>CSMS:</u> Monocations, m_1^+, formed in the ion source of a multi-sector mass spectrometer, are accelerated to several keV kinetic energy and mass-selected by means of a magnetic field B before colliding with a collision gas, preferably oxygen, in a collision cell located in the field-free region between B and the electric sector E. Charge-stripping peaks due to reaction (1) are obtained by scanning the electric sector voltage (E) around E/2, where E represents the voltage required to transmit stable m_1^+ ions. The displacement of the peak from 0.5 E reflects the tranlational energy loss (Q_{min}) in process (1) and corresponds to the ionization energy (IE) of m_1^+ (ref. 10 - 12). The ionization energies thus obtained can be compared with theoretically evaluated energies. Further characterization can be obtained by performing high level ab initio MO calculations (ref. 16).

$$m_1{}^+ + target \longrightarrow m_1{}^{2+} + target + e^- \qquad (1)$$
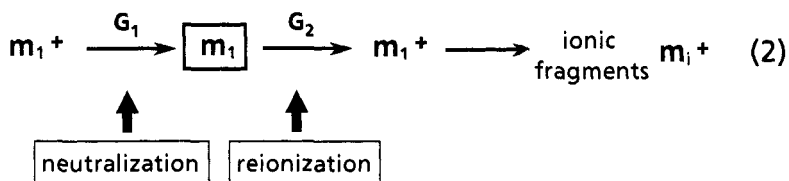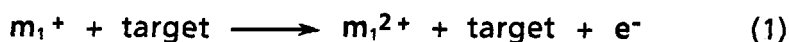
<u>NRMS:</u> The starting point is, again, a mono-cation, which after acceleration to typically 8 keV translational energy is mass selected and subjected to a sequence of collision experiments. The ion beam is first reduced by electron transfer from a suitable gas G_1 (Xe or metal atoms (Eq. 2)). All ions which have survived the neutralization step are deflected away from the molecular beam by a charged deflector electrode which is located between the two collision cells. The only species which enter the second collision cell are therefore the neutral molecule m_1 (having the momentum of m_1^+) and their uncharged dissociation products m_i (having the momentum m_i/m_1). The fast moving neutrals are reionized by collision with a target gas G_2 in the second chamber. This oxidation step should be performed in such a way that not only reionized molecular species m_1^+ but also charged, structure-indicative fragments are formed. The mass spectrum of the latter may serve to characterize m_1^+. Upon its generation in cell 1 it takes c. 10^{-6} s for m_1 to reach cell 2. The presence of a signal m_1^+ in the NR mass spectrum therefore signifies that the neutral m_1 has a lifetime $> 10^{-6}$ s. For further details, in particular for the suitability of various collision gases or the problem of generating ground versus excited states (see Ref. 13 - 15). In the present contribution a few examples are discussed to indicate the scope and limitations of both CSMS and NRMS.

## UNUSUAL NEUTRAL MOLECULES

Substituted acetylenes

All attempts to generate, in solution, stable acetylene derivatives XC≡CY (X = H; Y = OH, NH_2; X = Y = OH, NH_2) failed due to rapid intermolecular reactions. As has been shown recently (ref. 17 - 19) in the gas phase these novel molecules are easily accessible by NRMS. While hydroxyacetylene (HC≡COH)

and aminoacetylene ($HC\equiv CNH_2$), the latter being a potential interstellar mo-
lecule, can conveniently be generated by decarbonylation of propiolic acid
and its amide (Eq. 3), the consecutive losses of two CO molecules from squaric
acid and its derivatives (Eq. 4) is an easy entry for the generation of $XC\equiv CY$.
As indicated in Eqs. 3 and 4, the mono-cations $HC\equiv CX^{+\cdot}$ and $XC\equiv CY^{+\cdot}$ can also
serve as precursors to generate the analogous dications in CS experiments.

$$X = OH, NH_2 \tag{3}$$
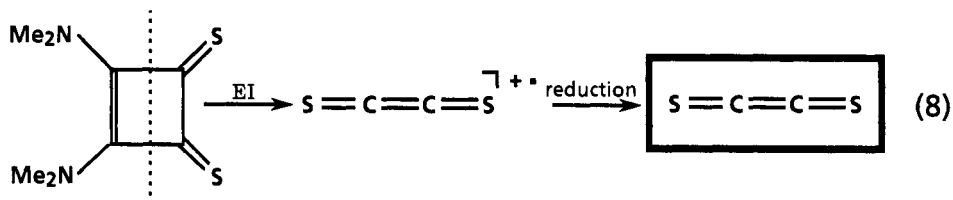

$$X = Y = OH, NH_2; \; X = OH; \; Y = NH_2 \tag{4}$$
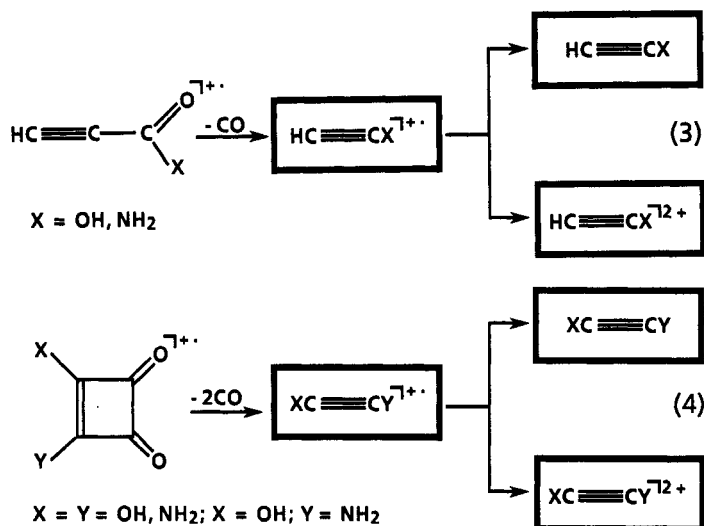
Carbonic acid, carbamic acid and sulfurous acid

Statements of the kind that "carbonic, $(HO)_2CO$, carbamic, NH_2CO_2H, and sulfu-
rous acids, $(HO)_2SO$, cannot exist in the free state" are warranted in so far
as it has not been possible to prepare these molecules as stable species in
solution. This is not due to an inherent instability of these molecules but
rather to the fact that, in solution, acid/base or solvent catalyses promote
a rapid decomposition and deprotonation. In the gas phase, however, quite a
different situation obtains: The unimolecular dissociations of the three
acids (i. e. losses of H_2O or NH_3, respectively,) are predicted by ab initio
MO studies to be hampered by significant barriers (>40 kcal/mol), and thus
the free acids should exist as stable molecules. Indeed, all three acids could
recently be generated and characterized both as neutral molecules as well as
cation radicals (Eq. 5 - 7) (ref. 20 - 22).

$$\tag{5}$$

$$\tag{6}$$

$$\tag{7}$$
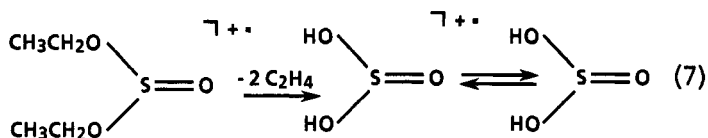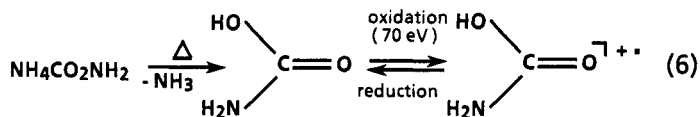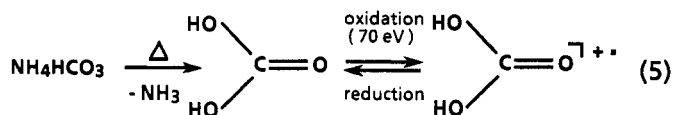
Ethylenedithione, (CS)$_2$, and ethylenedione, (CO)$_2$

High level ab initio calculations clearly predict (ref. 23) that both (CS)$_2$ and (CO)$_2$ should exist as stable molecules. However, all experimental attempts failed to make these species when "conventional" methods were employed. In contrast, the NRMS experiment proved once more its superiority (ref. 24, 25). Dissociative ionization of the tetramethyldithioamide of squaric acid yields in great abundance $C_2S_2^{+\cdot}$ which was readily neutralized to stable C_2S_2 (Eq. 3). The fact that the recovery signal in the NRMS experiment was unusually strong, points to the fact that the geometries of both neutral and ionized C_2S_2 should be quite similar; this is indeed corroborated by ab initio MO calculations (ref. 24).

$$\text{Me}_2\text{N} \underset{\text{Me}_2\text{N}}{\overset{\text{S}}{\bigsqcup}} \text{S} \quad \xrightarrow{\text{EI}} \quad [\text{S}=\text{C}=\text{C}=\text{S}]^{+\cdot} \quad \xrightarrow{\text{reduction}} \quad \boxed{\text{S}=\text{C}=\text{C}=\text{S}} \qquad (8)$$

For the generation of the long-sought after dimer of carbon monoxide, (CO)$_2$, a different approach had to be used, as dissociative ionization (cycloreversion processes), of potentially promising precursors did not result in the formation of a "clean" $(CO)_2^{+\cdot}$. The latter, however, is in principal accessible via clustering of $CO^{+\cdot}$ with neutral CO in a chemical ionization source (Eq. 9). If the so-formed $(CO)_n^{+\cdot}$ clusters (n = 2 - 10) are subjected to mass analysis at medium resolution, neutralization of, for example, clusters with n = 2,3,4 give indeed rise to survivor signals. However, exact mass measurements of these signals prove that they do not have the required elemental composition of C_2O_2 (m/z 56), C_3O_3 (m/z 84), and C_4O_4 (m/z 112), respectively, but rather contain spurious Fe! Thus, the existence of stable, neutral (CO)$_n$ (n = 2 - 4) is still awaiting experimental confirmation.

$$CO^{+\cdot} + m\,CO \longrightarrow (CO)_n^{+\cdot} \xrightarrow{\text{reduction}} \boxed{(CO)_n} \qquad (9)$$
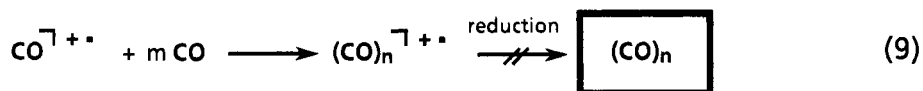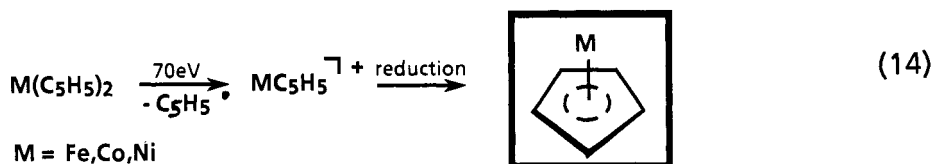
Electronically unsaturated organometallic fragments

Organometallic compounds produce ionic fragments through dissociative gas phase ionization (Eq. 10). NRMS experiments on these ions should establish whether the neutral analogues, ML$_n$, have sufficiently long lifetimes to allow investigations.

$$ML_n \xrightarrow[-L_m]{-e} ML_{n-m}^{+} \xrightarrow{\text{reduction}} \boxed{ML_{n-m}} \qquad (10)$$

Preliminary experiments justify cautious optimism in the direction of so far inaccessible, ligand-deficient neutral organometallic compounds. Two examples may suffice to illustrate the point.

Alkyl groups bonded to metals in varying states of saturation (MCH_x : M = transition metal atom or complex; x = 0-3) are commonly proposed intermediates in many homogeneous (ref. 26) and heterogeneous catalytic processes (ref. 27). In the condensed phase such species are far too reactive to study. NRMS, however, proved helpful (ref. 28) in that evidence was found for the existence of $FeCH_x$ (x = 1-3) and the ionic precursors $FeCH_x^+$. From the NR mass spectra it was further indicated that the tendency to isomerize $FeCH_x$ species to hydridometal species is dependent upon the degree of hydrogenation (Eq. 11 - 13).

$$Fe-CH_3 \rceil^{+,\circ} \quad \underset{?}{\overset{}{\rightleftharpoons}} \quad H-Fe\!\!=\!\!C\!\!\begin{array}{c}H\\H\end{array} \rceil^{+,\circ} \qquad (11)$$

$$Fe\!\!=\!\!CH_2 \rceil^{+,\circ} \quad \underset{?}{\overset{}{\rightleftharpoons}} \quad H-Fe\!\!\equiv\!\!C-H \rceil^{+,\circ} \qquad (12)$$

$$Fe\!\!\equiv\!\!CH \rceil^{+,\circ} \quad \underset{?}{\overset{}{\rightleftharpoons}} \quad H-Fe\!\!\equiv\!\!C \rceil^{+,\circ} \qquad (13)$$

$$M(C_5H_5)_2 \xrightarrow[-C_5H_5\bullet]{70eV} MC_5H_5 \rceil^+ \xrightarrow{reduction} \boxed{\begin{array}{c}M\\(\pm)\end{array}} \qquad (14)$$
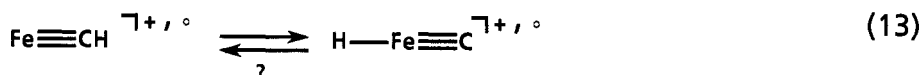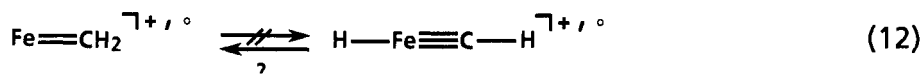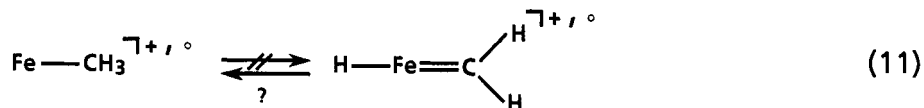
M = Fe, Co, Ni

Half-sandwich complexes of the type MC_5H_5 (M = Fe, Co, Ni) are well known in mass spectrometry (ref. 29, 30). In contrast, no examples seem to exist for the generation of a stable <u>neutral</u> MC_5H_5 molecule in solution. However, under NRMS conditions this can easily be achieved in that neutralization of $MC_5H_5^+$ generates strong survivor signals, and preliminary experiments point to a distinct role the metal atoms play in the efficiency of the reaction (Eq. 14). It was observed (ref. 31) that the intensity of the recovery signal for MC_5H_5 follows the trend $FeC_5H_5 < CoC_5H_5 < NiC_5H_5$ which might reflect the different binding energy between the metal and the C_5H_5 unit (ref. 32).

CHARGE STRIPPING EXPERIMENTS

In the preceding section it has already been mentioned that CS is an extremely convenient method to generate from a beam of solitary monocations the corresponding dications, and the examples given in Eq. 3,4 are illustrative cases. In fact, literally speaking hundreds of quite exotic dications were studied over the last decade (ref. 12,16,33 - 37), and the dications were rightly described as an "emerging class of remarkable molecules" (ref. 33). Salient features of these species, including stable molecules as small as He_2^{2+} (ref. 38), are the following ones: (1) Although most dications are thermochemically extremely unstable towards charge separation reactions (coulomb explosion), these reactions are very often prevented by significant barriers thus kinetically stabilizing the dications. (2) However, the prospects of generating in solution any of the small organic dications are extremely

remote. This is due to the fact that proton transfer from the dication to the solvent shell or addition of negatively charged species, like electrons, to the dication will occur avidly. (3) The relative stabilities of di-cationic isomers are frequently reversed when compared with their neutral or mono-charged counter-parts. (4) Signigicant structural changes are observed which often favour anti-van't Hoff geometries.

In this contribution only a few examples will be discussed; they may further illustrate the extraordinary potential of CSMS to generate and characterize dications in the gas phase.
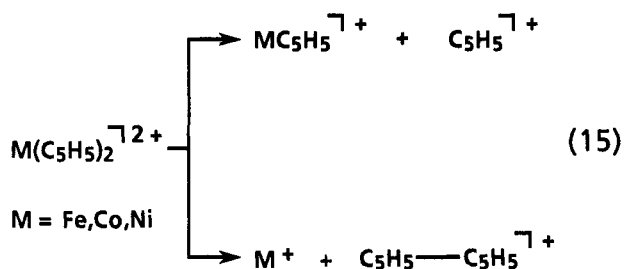
A) The coulomb explosion of doubly-charged sandwich compounds $M(C_5H_5)_2^{2+}$ (M = Fe,Co,Ni) was recently studied in detail (ref. 39). In addition to the "conventional" rupture of a metal-C_5H_5 bond, a rather unique reductive elimination of $M^{+\cdot}$ was observed for the first time (Eq. 15). Noteworthy is that in the course of the junction of the two C_5H_5 units, the Cp rings remain intact.

Chart 1 Hydride Dications XH_n^{2+}

X	H_1	H_2	H_3	H_4	H_5
C	a	+	+	+	+
Si	+	+	+	b	b
N	-	+	+	b	
O	-	+	+	b	
S	+	+	+		

^{a}Subject to controversy (see ref. 40)
^{b}Predicted to exist in minima

$$M(C_5H_5)_2^{2+} \longrightarrow \begin{cases} MC_5H_5^{+} + C_5H_5^{+} \\ \\ M^{+} + C_5H_5{-}C_5H_5^{+} \end{cases} \quad (15)$$

M = Fe,Co,Ni

B) The often noted reversal of stability when comparing neutral molecules with their analogous mono- and dicationic species also applies to the NBH_4 system, which was studied recently in a combined experimental/theoretical approach (ref. 40). Aminoborane (NH_2BH_2), the inorganic analogue of ethylene, and ammoniaborene (NH_3BH) were found to correspond to minima on the potential energy surfaces of the mono- and dications. While NH_2BH_2 is found to be more stable than NH_3BH, a reversal of stability is predicted for the mono- and dications. At the MP4/6-311G(d,p)//G-31G(d) + ZPE level of theory, $NH_3BH^{+\cdot}$ is 2.5 kcal/mol more stable than $NH_2BH_2^{+\cdot}$; the huge difference of 60.6 kcal/mol favouring NH_3BH^{2+} over $NH_2BH_2^{2+}$ was ascribed to a powerful donor/acceptor interaction operative in the former. Interestingly, charge stripping of $NBH_4^{+\cdot}$ leads exclusively to the formation of NH_3BH^{2+}, and the Q_{min} value of 15.2 eV is in excellent agreement with the theoretically predicted ionization energy.

It was recently demonstrated that systems with two-centre/three-electron S-S bonds are indeed viable species even under isolated conditions (ref. 41). Even more interestingly, oxidation to the dications can be achieved in the gas phase using CSMS (ref. 42), and the data given in Eq. 16 indicate that a

not yet fully understood correlation seems to exist between Q_{min} (i. e. the energy to remove an electron from the σ^*-orbital) and the λ_{max} values (which reflect the energy gap between the σ and σ^*-orbitals).

The last example is concerned with the controversially debated case of the $CH^{2+\cdot}$ dication (ref. 43). This dication belongs to the class of hydride dications (see Chart 1) for which quite a number of species could either be observed experimentally or were predicted by theory to have a finite lifetime (ref. 16).

650	600	525	470	450	440 nm	(16)
15,0	14,1	13,4	13,2	12,7	12,3 eV	
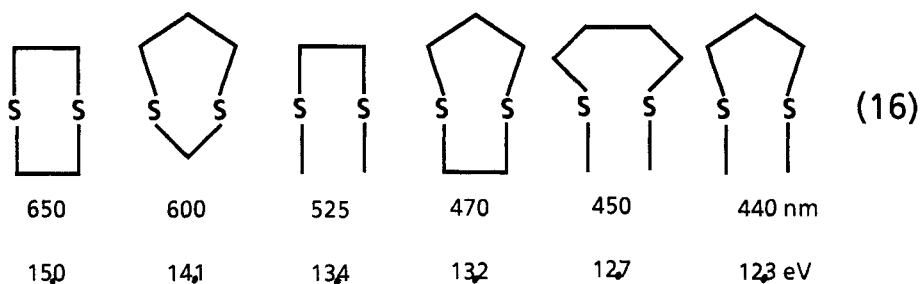
According to new (ref. 43) CS experiments and contrary to earlier reports there is no experimental indication for a metastable $CH^{2+\cdot}$. This result is supported by extensive new ab initio calculations (ref. 43) using a large Slater-type basis set on the three lowest $^2\Sigma^{+\cdot}$ states of $CH^{2+\cdot}$. Although the ground state potential curve is considerably perturbed by excited states, the perturbations are not sufficient to generate a potential minimum.

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