CHIMIA 39 (1985) Nr. 12 (Dezember)

Gaseous Organic Dications: Molecules with Remarkable Properties**

Wolfram Koch, Francis Maquin, Daniel Stahl, and Helmut Schwarz*

Dedicated to Professor Tino Gäumann on the occasion of his 60th birthday

Can small organic dications be generated in solution and/or the gas phase? What are the properties of these species with regard to their unimolecular chemistry (will they fall apart due to high Coulomb repulsion?) and their interaction with the solvent shell? What principles do they owe their existence to and what is the interplay of electrostatic repulsion versus binding energy? Answers to these and many other questions are provided by combined experimental/theoretical studies. In most cases pleasing agreement is observed which even includes the ionization energies of monocations from which dications are formed using charge-stripping mass spectrometry. Salient features of the doubly-charged cations are: 1) The often observed reversal of relative stabilities of isomers when compared with their neutral or mono-charged counterparts; 2) the significant structural changes which frequently favour anti-van't Hoff geometries; 3) the highly exothermic charge separation reactions which in the gas phase, however, are prevented by substantial barriers from occuring spontaneously, thus making observation of the thermochemically unstable dications feasible. The prospects of generating in solution any of the dications discussed are quite remote. Proton transfer from the dication to the solvent shell or addition of negatively charged species to the dication will occur avidly.

1. Introduction

Recent developments in mass spectrometry have led to new information about the gas phase properties of doubly-charged cations[1], which proved as an emerging class of remarkable molecules[2]. Although small dications have a tendency to fragment into two monocations because of Coulomb repulsion between the positive charges, experiments have clearly indicated that such doubly-charged species may persist for several microseconds[3]. Perhaps, the most exciting example concerns the recent[4] experimental detection of $He_2^{2\oplus}$, one of the smallest possible doubly-charged molecules, which has been generated and identified by charge-stripping (CS) mass spectrometry[1,5]. In $He_2^{2\oplus}$ electrostatic repulsion must be enormous. According to Coulomb's law, the energy released when two point charges of 0.704 Å apart (which corresponds to the calculated equilibrium distance of $He^{\oplus}$–$He^{\oplus}$) separate to infinity is 472 kcal/mol. Despite this huge driving force, $He_2^{2\oplus}$ is predicted theoretically to have a bound (metastable) ground state, $X^1\Sigma_g^+$, and the dissociation is inhibited by an energy barrier calculated to

* *Correspondence:* Prof. Dr. H. Schwarz
Institut für Organische Chemie
Technische Universität Berlin
Strasse des 17. Juni 135
D–1000 Berlin 12

Dr. D. Stahl
Institut de Chimie Physique
École Polytechnique Fédérale de Lausanne
ETH-Ecublens
CH–1015 Lausanne

** The continuous support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Fonds National Suisse pour la Recherche Scientifique is gratefully acknowledged. We are particularly indebted to the Computer Centres of TU Berlin and the Konrad-Zuse-Zentrum for providing generously computer time.

Helmut Schwarz: Born 1943 in Nickenich (Eifel). After having worked for 4 years as a technician in chemical industry (Dynamit Nobel AG, Troisdorf) training in chemistry at the Technische Universität Berlin (TUB), 1966–1971, where he received his Ph. D. with Ferdinand Bohlmann in 1972 and his Habilitation (organic chemistry) in 1974. In 1978 he was appointed to a Professor of Mass Spectrometry at TUB, and in 1983 he succeeded Albert Gossauer as a Professor of Organic Chemistry at TUB. H. Schwarz served as a Visiting Professor at the École Polytechnique Fédérale de Lausanne (1979) and the Hebrew University Jerusalem (1983). In 1981 he was elected Overseas Fellow of Churchill College, Cambridge, and in 1985 Forchheimer Professor of the Lady Davis Foundation, Israel. For his work (physical organic chemistry, mass spectrometry, elementary processes of ions, application of quantum chemistry) he has been awarded with the Dozentenstipendium des Fonds der Chemischen Industrie (1978) and the Otto-Klung-Preis (1982).

Wolfram Koch: Born 1959 in Darmstadt (Südhessen). Training in chemistry at both Technische Hochschule Darmstadt and Technische Universität Berlin, where he received his Diploma 1984 with Helmut Schwarz. He is presently working on his Doctoral Thesis, mainly dealing with quantum-chemical investigations.

Daniel Stahl: Born 1941 in Montbrison (France). Studied chemistry at the École Polytechnique de l'Université de Lausanne (now ETHL), graduated in 1967. Since 1969 at the Physical Chemistry Department of the ETHL, Ph.D. in mass spectrometry 1975, Lecturer in Physical Chemistry and Computer in Analytical Instrumentation since 1977.

Francis Maquin: Born 1954 in Boulogne-Billancourt (France). Studied biological engineering at the Université de Compiègne, graduated in 1978. DEA in Enzymatic Technology (Compiègne, 1979). From 1981 to August 1985 Assistant at the Physical Chemistry Department of the ETHL, Ph.D. in mass spectrometry 1984. Now he is working in pharmaceutical industry (Roussel-Uclaf, Romainville).

be 34.6 kcal/mol[6]. What is the nature of this barrier and to which principles do many other small dications owe their existence? The answer is surprisingly simple: For short increases in length from the equilibrium distance, the loss in binding energy (which follows roughly an r^{-2} function) is greater than the gain due to the reduction in electrostatic repulsion (which depends on r^{-1}). In fact, contrary to the common view that small multi-charged cations are intrinsically unstable, but in line with previous suggestions of *Dunitz* et al.[7], «that a bond may (even) be strengthened by effective positive charges on adjacent nuclei provided the charges are not too large», we and others[3] have indeed detected numerous small dications.

In this article[8] we present an overview of the joint work performed at the TU Berlin and the ETH Lausanne in which, by using a combined experimental/theoretical approach, small dications having remarkable properties, were generated and characterized in the gas phase. The examples discussed include various dications of hydrides, $XH_n^{2\oplus}$ (X = C,Si,N,O; n = 1–5), and some ylide dications, $CH_2XH^{2\oplus}$ (X = NH_2,OH, halogen, etc.). Special attention is paid to the unusual chemistry of the $CH_3O^{2\oplus\odot}$ and $C_2H_4O^{2\oplus}$ systems, which is also compared with the chemistry of the corresponding monocations and neutrals. In a further section we will discuss aspects of the chemistry of $C_2H_{4-n}F_n^{2\oplus}$ (n = 1–4), and in the concluding chapter some exotic systems are briefly discussed. We will also focus on questions like: (i) What are the structural changes when comparing M, $M^{\oplus\odot}$ and $M^{2\oplus}$? or (ii) Can small organic dications be generated in solution, and if so what is their fate likely to be?

2. Methodologies

To study dications in the gas phase the species of interest are generated from singly-charged precursors using charge-stripping mass spectrometry (CSMS). To this end, monocations $m_1^{\oplus}$ formed in the ion source of a double-focussing ZAB-2F mass spectrometer (BE configuration) using any of the many existing ionization methods, are mass selected by means of the magnet B before colliding with a collision gas, preferably oxygen, in the collision cell located in the second field-free region.

(1) $m_1^{\oplus}$ + target → $m_1^{2\oplus}$ + target + $e^{\ominus}$

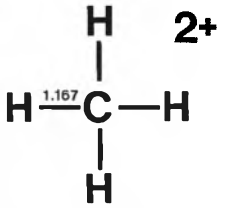
Charge-stripping peaks due to reaction (1) are obtained by scanning the electric sector (E) voltage around $E/2$, where E represents the voltage required to transmit stable $m_1^{\oplus}$ ions. The displacement of the peak from 0.5 E reflects the translational energy loss (Q_{min}) in process (1) and corresponds to the ionization energy (IE) of the monocation $m_1^{\oplus}$[1,9]. The ionization energies thus obtained can then be compared with theoretically evaluated energies. Further characterization of the gas phase species is achieved by performing high-level ab initio molecular orbital (MO) calculations, which in some cases fulfil the criterions of «state of the art» calculations.

Theory also proved to be able to answer a number of important questions, which cannot always be adequately dealt with experimentally, and which include information on the energetics of the species, their electronic structures, and their isomerization/dissociation pathways. For details of the charge stripping experiments as well as the calculations and further features of the respective ions studied, the reader is referred to the original papers.

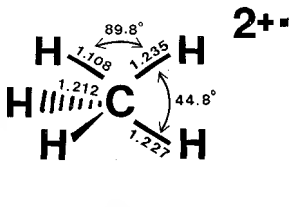
3. Dications of XH_n Hydrides (X = C,Si,N,O; n = 1–5)

Hydrocarbon dications, $CH_n^{2\oplus}$ (n = 1–5), were studied in great detail both experimentally[9–11] and theoretically[11,12]. Although there are some discrepancies between the theoretically predicted and the experimentally observed ionization energies for generating $CH_n^{2\oplus}$ from the corresponding monocations, it is now generally accepted that all these hydrides are stable species in spite of their high exothermicities in deprotonation reactions (see below).

From a structural point of view the most dramatic changes are found for the methane dications. While the neutral CH_4 has T_d symmetry and the cation radical, $CH_4^{\oplus\odot}$, has a C_{2v} structure, the global minimum of $CH_4^{2\oplus}$ corresponds to an anti-van't Hoff geometry of D_{4h} symmetry (**1**). Although dissociation of **1** to $H^{\oplus}$ and $CH_3^{\oplus}$ is exothermic by 106 kcal/mol, a barrier of 17 kcal/mol prevents **1** from dissociating spontaneously. Similarly, the «methonium» dication, $CH_5^{2\oplus\odot}$ (**2**), was observed experimentally[11]; a barrier of 24 kcal/mol separates **2** from its dissociation products $CH_4^{\oplus\odot}$ and $H^{\oplus}$ which are 77 kcal/mol below the energy of **2**. In **1** and **2** and most



1 (D_{4h})



2 (C_s)

other organic dications the charges are dispersed to the hydrogen periphery which is favoured both electrostatically and by the electropositive nature of hydrogen. The ionization needed to generate **1** and **2** from their corresponding mono-cations were measured[11] by CSMS to be 18.9 and 21.6 eV, respectively, which is in good agreement with the theoretically evaluated adiabatic ionization energies.

Silicon hydride dications, $SiH_n^{2\oplus}$ (n = 1–5), were studied both theoretically[13,15] and experimentally[13,14]. While there exist some analogies there are also distinct differences when $SiH_n^{2\oplus}$ are compared with the analogous $CH_n^{2\oplus}$ species. For example, like most small dications, the $SiH_n^{2\oplus}$ species are thermochemically highly unstable but, are nevertheless prevented by energy barriers from dissociating spontaneously to form singly-charged cations. However, the instabilities of the $SiH_n^{2\oplus}$ species (indicated by the enthalpies of the deprotonation reactions of the processes $SiH_n^{2\oplus} \rightarrow SiH_{n-1}^{\oplus} + H^{\oplus}$) turn out to be less pronounced than for their carbon counterparts (see Table 1). This is a direct consequence of the better capability of silicon to accomodate the positive charge which itself is due to its lower electronegativity and higher polarizability compared with carbon.

Table 1. Calculated energies (kcal/mol) for the processes $XH_n^{2\oplus} \rightarrow XH_{n-1}^{\oplus} + H^{\oplus}$ (X = C, Si)[13].

Molecule	Deprotonation Energy X = Si	X = C
$XH_5^{2\oplus\odot}$	− 13.4	− 77.0
$XH_4^{2\oplus}$	− 26.1	− 105.7
$XH_3^{2\oplus\odot}$	− 48.0	− 108.5
$XH_2^{2\oplus}$	− 20.0	− 71.4
$XH^{2\oplus\odot}$	− 35.4	− 147.5

From the theoretically predicted[13] five stable $SiH_n^{2\oplus}$ dications (n = 1–5) the species $SiH^{2\oplus\odot}$, $SiH_2^{2\oplus}$, and $SiH_3^{2\oplus\odot}$ were indeed observed experimentally[13b,14]. Again, a comparison with the valence isoelectronic $CH_n^{2\oplus}$ dications is revealing. While $CH^{2\oplus\odot}$ has a purely repulsive ground state, or at most a very shallow energy dip, the $X^2\Sigma^+$ ground state of $SiH^{2\oplus\odot}$ lies in a deep well separated by a barrier of > 20 kcal/mol from the charge separation products[15].

There is both experimental and theoretical evidence that also the first excited state of $SiH^{2\oplus\odot}$, i.e. $A^2\Pi$, exists as a stable species. When the dissociation reaction $SiH^{2\oplus\odot} \rightarrow Si^{\oplus\odot} + H^{\oplus}$ is monitored a peak shape («composite peak») analysis of the kinetic energy releases associated with the formation of $H^{\oplus}$ and $Si^{\oplus\odot}$ indicates that the intercharge distances $Si^{\oplus}...H^{\oplus}$ of the two singly-charged species at the time of separation are ca. 6 Å for the $X^2\Sigma^+$ state of $SiH^{2\oplus\odot}$ and 1.7 Å for the $A^2\Pi$ state, in good agreement with theoretical predictions[15].

For $SiH_2^{2\oplus}$ the most stable species corresponds to the linear singlet structure **3**, which is also prevented by a large barrier from deprotonation. The open-shell dication $SiH_3^{2\oplus\odot}$ is, like $CH_3^{2\oplus\odot}$, Jahn-Teller distorted from the planar D_{3h} symmetry. The most stable structure for $SiH_3^{2\oplus\odot}$ (**4**) can be understood as a loosely-bound complex of $SiH_2^{2\oplus}$ and $H^{\odot}$, which is indicated by both the geometrical features of **3** and **4** and the fact that 86% of the positive charges of **4** are located in the «SiH_2» moiety. The higher $SiH_n^{2\oplus}$ species (n = 4,5), are as yet unobserved due to the lack of suitable precursors. These dications can also be viewed as complexes of $SiH_2^{2\oplus}$ with H_2 and $H^{\odot}$, respectively. For $SiH_4^{2\oplus}$ the global minimum corresponds to **5** (which is predicted to be more than 65 kcal/mol more stable than the D_{4h} isomer; in fact, $SiH_4^{2\oplus}$ with D_{4h} symmetry is not a true minimum as the Hessian matrix has two negative eigen values. Note, that for $CH_4^{2\oplus}$ it is the D_{4h} species which is the more stable one!). For $SiH_5^{2\oplus\odot}$ several species were located on the potential energy surface. At the MP4/6–31G**//6–31G* level of theory, **6** – a weak complex of $H^{\odot}$, H_2, and $SiH_2^{2\oplus}$ – is predicted to be the global minimum.

Among the dications of oxygen hydrides, $OH_n^{2\oplus}$ (n = 1–4), the only species so far detected experimentally[3,16] is that of $OH_3^{2\oplus\odot}$, which is easily accessible by charge-stripping from $H_3O^{\oplus}$ with an ionization energy of 23.5 eV. $OH_3^{2\oplus\odot}$ (D_{3h}),

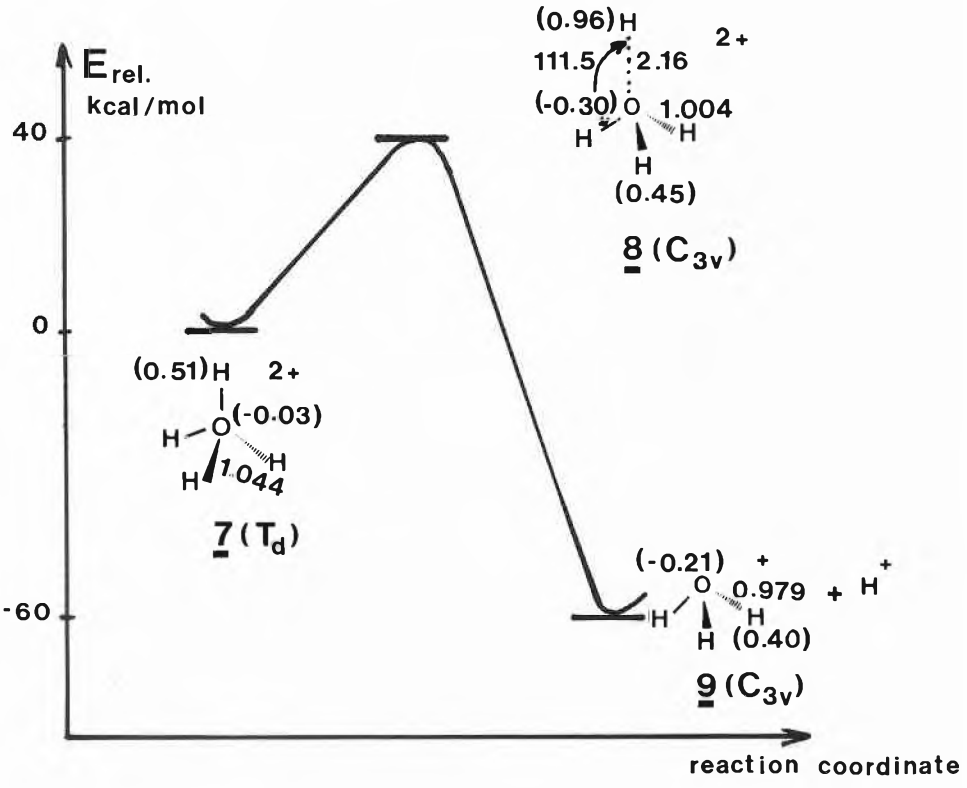


*Fig. 1. Potential energy diagram (MP4/6–311++G**//MP2/6–31G*) for $H_4O^{2\oplus} \rightarrow H_3O^{\oplus} + H^{\oplus}$. Bond lengths in Å, bond angles in degrees, numbers given in parentheses refer to charges.*

isoelectronic with $CH_3^{\oplus}$, exists in a deep potential well. Although the reaction $OH_3^{2\oplus\odot} \rightarrow OH_2^{\oplus\odot} + H^{\oplus}$ is exothermic by -87 kcal/mol[3], spontaneous dissociation is not possible because of the existence of a large barrier (21 kcal/mol). The ground-state potential energy surface of $OH^{2\oplus\odot}$ is according to high-level calculations purely repulsive[3,17], thus explaining the experimental finding that no stable $OH^{2\oplus\odot}$ could be detected. The result, that $OH_2^{2\oplus}$ escaped experimental verification is due to the fact that both the singlet (C_{2v}) and triplet ($D_{\infty h}$) states of $OH_2^{2\oplus}$ are prone to dissociate to $H^{\oplus}$ and $OH^{\oplus}$ via barriers as small as 2.5 and 1.5 kcal/mol. The most spectacular dication among the oxygen hydrides is, undoubtedly, that of $OH_4^{2\oplus}$ (**7**), which is isoelectronic with methane. As is the case with $OH_3^{2\oplus\odot}$ the charges in **7** are dispersed to the hydrogen periphery ($+0.51$ per hydrogen) and the oxygen is even found to be slightly negatively charged (-0.03) (Fig. 1). Species **7**, which due to the lack of a precursor has not yet been generated experimentally, is predicted[3,18] to reside in a very deep potential well. Deprotonation, via **8**, in the gas phase requires 40 kcal/mol, although the reaction is exothermic by -59 kcal/mol.

While $OH_3^{2\oplus\odot}$ is found to exist and $OH_4^{2\oplus}$ predicted to be stable in the gas phase, both species are very unlikely to ever be generated as viable dications in solution because of their extremely high thermochemical instability. The enthalpy of formation of $OH_3^{2\oplus\odot}$ is estimated to be 685 kcal/mol, and that of $OH_4^{2\oplus}$ to be 564 kcal/mol. Moreover, the disproportionation reactions (2) and (3) have enthalpies of reaction, ΔH_r°, of -253 and -225 kcal/mol, respectively. These were evaluated by isodesmic substitution at the MP4SDTQ/6–311++G**+ZPE level of theory. Thus, even if $OH_3^{2\oplus\odot}$ and $OH_4^{2\oplus}$ could be generated in solution they would immediately either transfer a proton to their solvent shell or strip a negatively charged particle from it[18].

		ΔH_r° [kcal/mol]
(2)	$H_3O^{2\oplus\odot} + H_2O \rightarrow H_2O^{\oplus\odot} + H_3O^{\oplus}$	-253
(3)	$H_4O^{2\oplus} + H_2O \rightarrow 2H_3O^{\oplus}$	-225

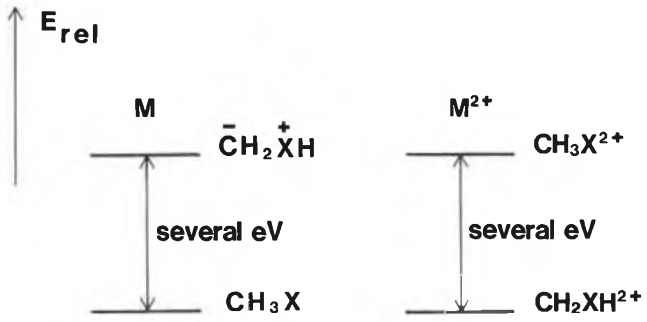
For the $NH_n^{2\oplus}$ series (n = 1–4) theory[17,19] and experiment[18] agree that only $NH_2^{2\oplus\odot}$ and $NH_3^{2\oplus}$ are experimentally accessible by charge stripping mass spectrometry. The non-existence of $NH^{2\oplus}$ is caused by the fact, that this dication, like $OH^{2\oplus\odot}$ and $CH^{2\oplus\odot}$, has a repulsive potential energy surface; for $NH_4^{2\oplus\odot}$, however, the absence of any stable species is due to a different origin: Vertical ionization of $NH_4^{\oplus}$ would lead to a state well above the energy of the transition state for deprotonation of $NH_4^{2\oplus\odot}$. In solution, *none* of the $NH_n^{2\oplus}$ (n = 1–4) dications is predicted to be stable. Like the $OH_n^{2\oplus}$ system, proton transfers to the solvent shell are extremely exothermic and will occur with avidity[19].

4. Ylide Dications, $CH_2XH^{2\oplus}$ (X = F,Cl,Br,I,OH,SH,NH_2)

There has been considerable recent theoretical and experimental interest in the gas phase chemistry of ionized ylides, $CH_2XH^{\oplus\odot}$, which can also be formally viewed as ion/dipole complexes between $CH_2^{\oplus\odot}$ and polar molecules XH[20]. The thermochemical and kinetic stabilities of $CH_2XH^{\oplus\odot}$ ions are usually comparable to – if not larger than – those of their isomeric forms $CH_3X^{\oplus\odot}$. This is in distinct contrast to the behaviour of the *neutral* parent molecules, the ylides $H_2C^{\ominus}-{}^{\oplus}XH$, which, in most known cases, do not exist as stable entities[21]; instead, they either isomerize via 1,2 hydrogen shifts to the substantially more stable CH_3X molecules or they fall apart to CH_2 and XH. Thus, ionization leads to a strong relative stabilization of the ylide structure $CH_2XH^{\oplus\odot}$. What might happen when a further electron is removed, i.e. the formation of the dications $CH_2XH^{2\oplus}$ and $CH_3X^{2\oplus}$, respectively, has been investigated for X = OH with the aid of high-level ab initio MO calculations[22] and for this and the other analogues experimentally by CSMS[22b]. Singlet $CH_3OH^{2\oplus}$ is not found to be a stationary point on the potential energy surface; it rearranges spontaneously to a weakly bound complex $H_2\ldots CH-OH^{2\oplus}$, which dissociates via a small barrier of < 3 kcal/mol into H_2 and $CHOH^{2\oplus}$. In distinct contrast, the dication $CH_2OH_2^{2\oplus}$ exists in a deep potential well; it is calculated to be more than 74 kcal/mol more stable than the $H_2\ldots CHOH^{2\oplus}$ complex and to be prevented from undergoing exothermic dissociations to, for example $CH_2^{\oplus\odot}$ and $OH_2^{\oplus\odot}$ or $CH_2{=}OH^{\oplus}$ and $H^{\oplus}$, respectively, owing to substantial barriers (89 and 60 kcal/mol).

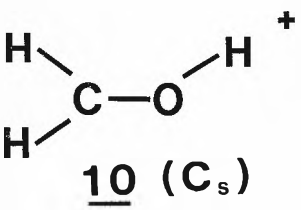
Similar situations prevail for the other $CH_2XH^{2\oplus}$ species. Charge stripping of the corresponding $CH_2XH^{\oplus\odot}$ gives rise to the formation of stable $CH_2XH^{2\oplus}$ with ionization energies ranging from 16.3 eV (for X = I) to 19.8 eV (for X = SH). Charge stripping from the isomeric $CH_3X^{\oplus\odot}$ monocations, however, is interpreted as a process in which the electron ejection is associated with (or followed by) isomerization to stable $CH_2XH^{2\oplus}$ rather than formation of unstable $CH_3X^{2\oplus}$. Thus, removal of two electrons produces fundamental changes in the stability order, a situation chemists are well aware of (aromatic versus anti-aromatic systems; conrotatory versus disrotatory processes; *nido*- versus *arachno*-structures, etc.): We note that while for the neutral molecules M the CH_3X species are invariably the most stable isomers, for the dications $M^{2\oplus}$ they do not any longer exist; the global minimum corresponds to the ylide-like structures $CH_2XH^{2\oplus}$ (Scheme 1).

Scheme 1

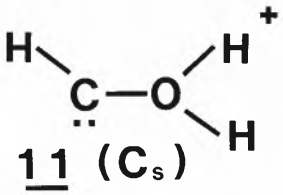


5. The $CH_3O^{2\oplus\odot}$ Potential Energy Surface

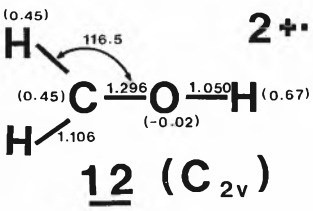
The reversal of stability discussed in the preceding section for the CH_3X/CH_2XH versus $CH_3X^{2\oplus}/CH_2XH^{2\oplus}$ systems was also found for the mono- and dications of species with the elemental composition CH_3O[23]. For the monocations it is firmly established that the most stable form is the hydroxymethyl cation (**10**) (*O*-protonated formaldehyde); the oxoniamethylene cation (**11**), for which no experimental observation has yet been reported, is predicted[24] to be 78 kcal/mol less stable than **10**. However, spontaneous isomerization **11**→**10** is hindered by a barrier as high as 30 kcal/mol. For the dications it is found at all levels of theory used, that the global minimum corresponds to **13** which is, calculated at the highest level of theory used (MP2/6–31G**//6–31G + ZPE), to be 23 kcal/mol more stable than **12**. Isomerization **12**→**13** would require an activation energy of 24 kcal/mol. As with other dications, the positive charges are dispersed substantially to the hydrogen periphery (see numbers given in parentheses of structures **12** and **13**). The quite short C–O bond distances for both dications, 1.296 Å and 1.308 Å, are certainly due to electrostatic attraction between the positively charged carbon and the negatively charged oxygen atoms. In the isoelectronic vinyl



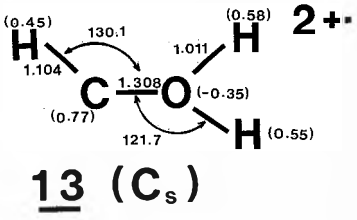
10 (C_s)



11 (C_s)



12 (C_{2v})



13 (C_s)

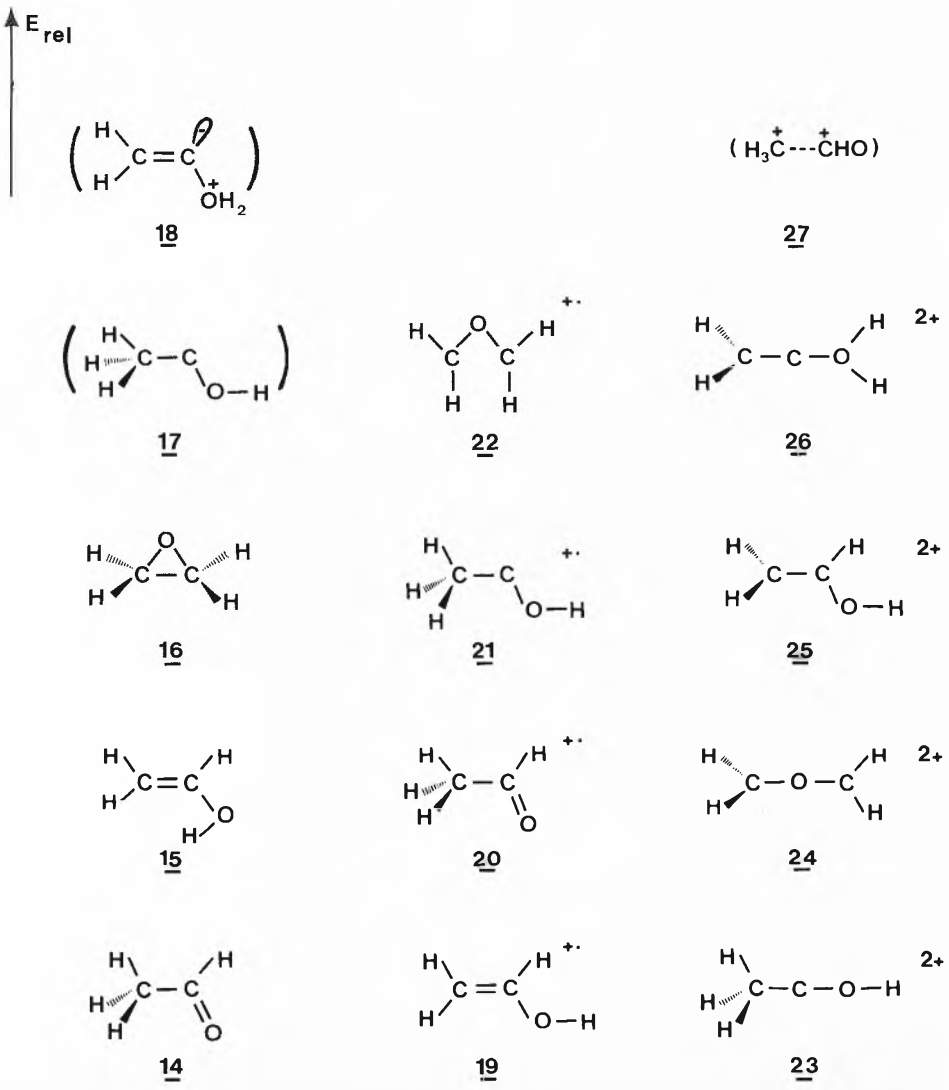
radical, the C–C bond is, with 1.339 Å (6–31G), significantly larger.

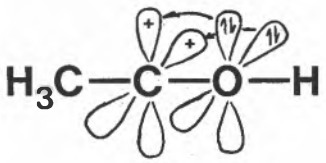
The energy needed to generate **12** from **10** in the gas phase by charge-stripping was determined to be 22.4 eV which is in good agreement with the calculated vertical ionization energy of 22.2 eV[23]. The enthalpy of formation of **12** was estimated to be 668 kcal/mol which corresponds well with an experimentally derived number of 659 kcal/mol, obtained from appearance energy measurements[25] for generating $CH_3O^{2\oplus\odot}$ from methanol. Because of the lack of suitable precursor molecules no experimental data are available for **13**. With regard to the thermodynamic and kinetic stabilities of **12** and **13**, theory clearly shows that in solution both species are unlikely to ever be generated as viable intermediates. Charge separation via proton transfer is very exothermic. In the gas phase, however, not only is interconversion of **12** and **13** hindered by a significant barrier; but also computational studies have shown that unimolecular dissociations to various products involve relatively high barriers. Thus, it is not surprising that a stable $CH_2OH^{2\oplus\odot}$ was indeed detected experimentally[23,25].

6. Isomeric $C_2H_4O^{2\oplus}$ Species

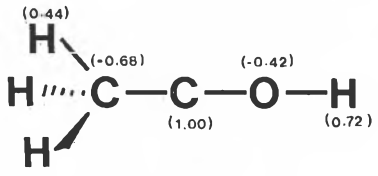
Significant structural changes associated with successive electron removals were also observed for the C_2H_4O system, which was extensively studied both experimentally and theoretically[26]. While for the neutral C_2H_4O system acetaldehyde (**14**) forms the global minimum, on the $C_2H_4O^{2\oplus}$ potential energy surface a stable dication **27** does not exist at all; electron removal from the monocation **20** by charge-stripping is associated with the formation of $CH_3^{\oplus}$ and $HCO^{\oplus}$. The as yet unknown neutral hydroxy(methyl)carbene (**17**) is, upon removal of two electrons transformed to a dication **23** which corresponds to the global minimum on the $C_2H_4O^{2\oplus}$ potential energy surface. Similarly, the unknown ylid **18** is predicted to form a stable dication **26**. Ethylene oxide (**16**) is, upon removal of two electrons transformed to **24**, which – like **26** – is isoelectronic with allene. Removal of two electrons from planar vinyl alcohol (**15**) results in the formation of a perpendicular dication **25** (both *syn*- and *anti*-conformations of the OH group are predicted to exist as stable species).

The origins of these structural changes and stabilization effects are manifold. The preference of the perpendicular form of the vinyl alcohol dication is, as it is for the ethylene dication itself (see next section), due to hyperconjugation which results in the best charge distribution. Removal of two electrons from the C–C π-orbital of **15** results in two formally vacant orbitals at the carbon atoms, which in the orthogonal structure interact hyperconjugatively with the corresponding C–H bonds. The planar form, which corresponds to the transition state for rotation around the C–C bond of **25**, lacks this kind of stabilization and is 5 kcal/mol less stable than **25** (MP2/6–31G*//4–31G + ZPE). A similar stabilization effect is operative for **24**. The global minimum on the $C_2H_4O^{2\oplus}$ potential energy surface, i.e. **23**, which is isoelectronic with propyne, gains its stability from two effects: (i) As shown by structure **23a**, the doubly-occupied p_y and p_z orbitals of oxygen interact strongly with the empty orbitals of C(1), thereby generating a formal C–O *triple* bond, comparable to the C–C triple bond of propyne. In fact, the C–O bond length of **23** is calculated (4–31G) to be as short as 1.13 Å. (ii) The strongly alternating charge distribution (6–31G*//4–31G) of **23** (see structure **23b**) induces a substantial electrostatic attrac-





23a



23b

tion within the C–C–O skeleton, which also stabilizes the dication.

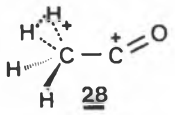
Further exploration of the $C_2H_4O^{2\oplus}$ potential energy revealed that most of the $C_2H_4O^{2\oplus}$ dications are prevented by barriers from both facile interconversion or unimolecular dissociation. Thus, experimental observation of $C_2H_4O^{2\oplus}$ should be feasible. In fact, charge stripping mass spectrometry provided evidence[26a] that **23**, **24**, and **25** can indeed be generated, and a comparison of the experimentally derived and theoretically predicted vertical ionization energies showed good agreement for **24** and **25** (see Table 2). For **23** the ionization energy could not be determined due to sensitivity problems.

The extreme thermodynamic instability of **23**, **24**, and **25**, indicated by their high enthalpies of formation and the exothermic disproportionation reactions (**4**)–(6) (6–31G*//4–31G) make it, however, highly unlikely that these dications can ever be formed as stable species in solution. Protonation of the solvent shell, electron capture, or hydride transfer from an adjacent neutral (or anion) will take place with avidity.

Table 2. Thermochemical data from some $C_2H_4O^{2\oplus}$ species.

		IE_{exp} [eV]	IE_{calc}	$\Delta H^\circ_{f,calc}$ [kcal/mol]
$CH_3COH^{2\oplus}$	(**23**)	–	–	554
$CH_2OCH_2^{2\oplus}$	(**24**)	16.3	15.6	574
$CH_2C(H)OH^{2\oplus}$	(**25**)	17.1	17.2	575

(7) $CH_4^{2\oplus} + CO \rightarrow$ **28** $\rightarrow H_2 + CH_2{=}C{=}O^{2\oplus}$



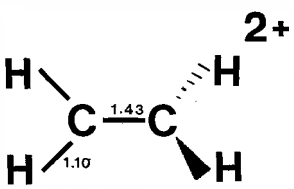
28

7. Ethylene and Fluorine Substituted Ethylene Dications, $C_2H_{4-n}F_n^{2\oplus}$ (n = 0–4)

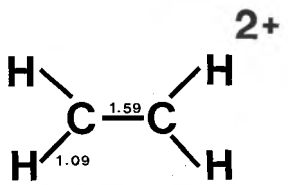
Ethylene and its dication provide a further case in point for structural changes associated with electron removal. $C_2H_4^{2\oplus}$ has been thoroughly studied both theoretically[28] and experimentally[29]. The anti-van't Hoff perpendicular (D_{2d}) conformer **29** is the global and the only singlet $C_2H_4^{2\oplus}$ minimum, being 28 kcal/mol (3–21G//3–21G) more stable than the planar D_{2h} structure **30** which corresponds to a rotational transition state. The source of stability of **29** over **30** is due to hyperconjugation. In the D_{2d} conformer the two formally vacant orbitals at the carbon atoms are orthogonal and each interact hyperconjugatively with the corresponding vicinal CH_2 groups. This leads to the best charge distribution; the positive charge is deflected to the periphery of the dication and resides primarily on the more electropositive hydrogen atoms. **30** lacks this stabilization; consequently it is much higher in energy, and also has a distinctly different geometry (see for example the C–C bond length; 6–31G*).

		ΔH_r° [kcal/mol]
(4)	$CH_3{-}C{-}OH^{2\oplus} + CH_4 \rightarrow CH_3CHOH^{\oplus} + CH_3^{\oplus}$	– 160
(5)	$CH_2{-}O{-}CH_2^{2\oplus} + CH_4 \rightarrow CH_3{-}O{-}CH_2^{\oplus} + CH_3^{\oplus}$	– 139
(6)	$CH_2{-}CHOH^{2\oplus} + CH_4 \rightarrow CH_3CHOH^{\oplus} + CH_3^{\oplus}$	– 154

A highly-interesting $C_2H_4O^{2\oplus}$ species was recently described in a theoretical study[27], in which it was shown that **28** also corresponds to a minimum on the potential energy surface of $C_2H_4O^{2\oplus}$. It is, however, doubtful whether **28**, a cation-substituted «methonium» ion, can be formed as suggested by either combining CO with $CH_4^{2\oplus}$ or by hydrogenation of the ketene dication. While these two reactions (7) are exothermic, they would have to compete with energetically equally feasible electron transfer processes leading to monocharged species.

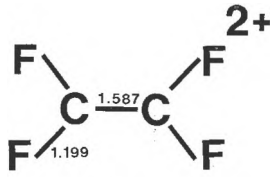


29(D_{2d})

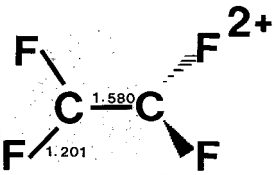


30(D_{2h})

What happens when the hydrogen atoms are replaced by fluorine, which is known not to stabilize cationic centres hyperconjugatively, has been recently studied theoretically and experimentally[30]. Replacement of all four hydrogen atoms in ethylene by fluorine atoms results in dramatic changes[30a]: (i) The global and the only minimum on the $C_2F_4^{2\oplus}$ potential surface corresponds to the planar D_{2h} form (**31**), which is 2.3 kcal/mol (MP3/6–31G**//6–31G*) more stable than the perpendicular D_{2d} structure (**32**); the latter is the transition state for the rotation around the C–C bond. (ii) In line with the relatively small energy difference between **31** and **32** the geometric features (6–31G*) of the two species are also comparable in distinction to the $C_2H_4^{2\oplus}$ system. In either form the charges are mainly located on the carbon atoms which – because of high Coulomb repulsion – leads to long C–C bonds; these are for both **31** and **32** longer than the one calculated for $C_2F_4^{\oplus\odot}$ (1.39 Å) and C_2F_4 (1.30 Å). Conversely, the decrease of the C–F bond lengths for **31** and **32**, relative to $C_2F_4^{\oplus\odot}$ (1.28 Å) and C_2F_4 (1.33 Å), points to a mesomeric contribution of the lone-pair electrons of fluorine which interact with the formally empty orbitals at the carbon atoms to generate a C–F «double»-bond. Replacement of the hydrogen atoms by fluorine atoms has no significant effect on the ionization energies. Electron loss from $C_2H_4^{\oplus\odot}$ requires 17.8 eV[29b] and for $C_2F_4^{\oplus\odot}$ the energy was determined to be 19.0 eV[30a]. For other $C_2H_{4-n}F_n^{\oplus\odot}$ species the following results were obtained: $C_2H_3F^{\oplus\odot}$: 18.7 eV, $CH_2CF_2^{\oplus\odot}$:18.7 eV, and $CHFCF_2^{\oplus\odot}$: 20.4 eV[31].



31(D_{2h})



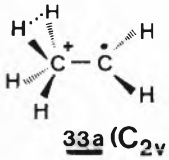
32(D_{2d})

With regard to the preferred conformation (planar versus perpendicular) of the $C_2H_{4-n}F_n^{2\oplus}$ species (n = 1,2,3), it was not surprising to learn that the energy differences between the two conformers are small, and favouring one over the other form is also dependent on the substitution pattern. A detailed analysis revealed[30b] that it is the interplay of C–H hyperconjugation, fluorine lone-pair donation, and C–F double-bond conjugation which determines which conformation is actually preferred. The theoretical results predict that $C_2F_4^{2\oplus}$ and $C_2HF_3^{2\oplus}$ prefer a planar conformation while for $C_2H_4^{2\oplus}$, $C_2H_3F^{2\oplus}$, and 1,1-$C_2H_2F_2^{2\oplus}$ the perpendicular form is the more stable one. However, the energy difference ranges from 30 kcal/mol (for $C_2H_4^{2\oplus}$) to only 2.3 kcal/mol (for $C_2F_4^{2\oplus}$).

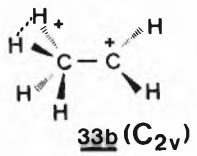
What should also be mentioned is the fact that in spite of the high Coulomb repulsion, dissociation of $C_2H_{4-n}F_n^{2\oplus}$ via charge separation reactions must be prevented by substantial barriers because all dications were observed in the gas phase.

8. Miscellaneous

The tempting suggestion[32] that the $C_2H_6^{2\oplus}$ species might have the structure of a carbenium-carbonium ion (**33b**) has encouraged experimentalists to search for evidence of this ion. In fact, charge-stripping of $C_2H_6^{\oplus\odot}$ results in the formation of a stable $C_2H_6^{2\oplus}$ and the energy for removing the electron was measured to be 18.4 eV[33]. *Beynon* et al. reported[34] the existence of two distinguishable $C_2H_6^{\oplus\odot}$ monocations, one being formed by electron impact ionization of C_2H_6 and the other via ion/molecule reactions of $CH_4^{\oplus\odot}$ with CH_4. The latter reaction is believed[34] to yield the complex **33a**, which upon charge-stripping might indeed result in the formation of **33b**. In fact, the ionization energy to remove an electron from **33a** (19.4 eV) is different from that measured for the oxidation of ionized ethane (18.4 eV), which together with the different collision-induced dissociation pattern could be interpreted as an indication that one is dealing with two different $C_2H_6^{\oplus\odot}$ species. It should, however, be mentioned that all our attempts failed to reproduce the results reported by *Rabrenovič* and *Beynon*[34].



33a (C_{2v})

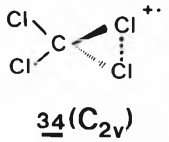


33b (C_{2v})

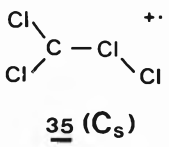
Dication **33b** owes its stabilization (i) to hyperconjugative interaction between the nominally vacant p orbital and the pyramidal CH_4 moiety, and (ii) to electrostatic effects. In **33b** the hydrogen atoms which carry most of the charges, are on average further apart than in other possible $C_2H_6^{2\oplus}$ structures[35], thereby reducing electrostatic repulsion.

Among the many halocarbon ions studied, a few selected examples will be briefly mentioned. For the simple $CX^{\oplus}$/$CX^{2\oplus}$ systems (X = F,Cl,Br) it was shown experimentally[36] that the monocations exist in both the ground state and long-lived electronically excited states. The separation between the two states is ≈ 5.0 eV (X = F), ≈ 2.7 eV (X = Cl), and ≈ 1.0 eV (X = Br). Charge-stripping from either state is believed to yield ground-state $CX^{2\oplus}$. Detailed theoretical studies were performed for $CF^{2\oplus}$ and $CF_2^{2\oplus}$[37]; it was shown that both dications are extremely stable species in spite of strong Coulomb repulsion. The analysis further revealed that the C–F bond contains high π-bond character due to the interaction of the fluorine lone-pair with the empty p orbital of the carbon atom, i.e. $C{=}F^{2\oplus\odot}$. The C–F bond distance of 1.146 Å (MP2/6–31G*) for $CF^{2\oplus\odot}$ is the shortest CF bond length ever reported. For $CF^{\oplus}$ and $CF^{\odot}$ the respective values are 1.173 and 1.291 Å. In $CF_2^{2\oplus}$ bonding is found to be slightly weaker than in $CF^{2\oplus\odot}$, but nevertheless remarkably strong. The increase in bond strength when going from CF_2 to $CF_2^{\oplus\odot}$ and $CF_2^{2\oplus}$ is reflected in the descreasing bond length (1.315, 1.232, and 1.166 Å) and also in the substantially higher vibrational frequencies, calculated for the C–F stretching vibrations (for example CF stretch (asym.) in CF_2:1391 cm^{-1}, $CF_2^{\oplus\odot}$:1851 cm^{-1}, and $CF_2^{2\oplus}$: 2486 cm^{-1}).

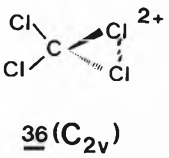
Recent experimental and theoretical work has provided evidence that the long-sought $CCl_4^{\oplus\odot}$ exists in two distinguishable isomeric forms, **34** and **35**[38]. Evidence was also presented for a stable $CCl_4^{2\oplus}$[39], and MO calculations suggested the C_{2v} form (**36**) to be the global minimum on the $CCl_4^{2\oplus}$ potential energy surface, being 84 kcal/mol more stable than the planar D_{4h} isomer (**37**). Experimental studies towards a $CCl_4^{2\oplus}$ dication structurally related with **35** are under way[40].



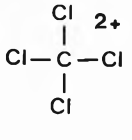
34 (C_{2v})



35 (C_s)



36 (C_{2v})



37 (D_{4h})

Among the small oxygen-containing organic dications we have studied, the following systems deserve brief mentioning: $CH_2O^{2\oplus}$, $C_2H_2O^{2\oplus}$, and $C_2H_3O^{2\oplus\odot}$.

In line with theoretical predictions[41] the hydroxymethylene dication (**38**), which can be described as a dicationic analogue of acetylene, was shown to be stable in the gas phase, while the isomeric formaldehyde dication, $CH_2O^{2\oplus}$, is not[42]. It was further demonstrated by studying labeled compounds that deprotonation of **38** involves specifically the hydroxy group; cleavage of the H–C bond of **38** would require a significantly larger activation energy (cf. (8)).

(8) $H{-}C{-}OH^{2\oplus}$ **38** ($C_{\infty v}$)

	ΔH_r° [kcal/mol]
E_0 = 46 kcal/mol → $H^{\oplus} + C{\equiv}\overset{\oplus}{O}{-}H$	− 35
E_0 = 22 kcal/mol → $H{-}\overset{\oplus}{C}{=}O + H^{\oplus}$	− 69

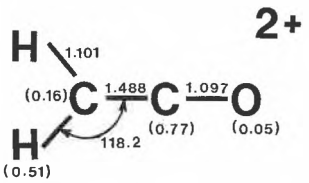
Finally, pleasing agreement between theory and experiment was also found for the transition state of the charge-separation reaction $HCOH^{2\oplus} \rightarrow HCO^{\oplus} + H^{\oplus}$. The intercharge distance, r, at the time of separation of the two departing monocations is, to a first approximation, related to the kinetic energy relases, T, by the simple equation (9)[43].

$$(9)\quad T[\text{eV}] = \frac{14.4}{r[\text{Å}]}$$

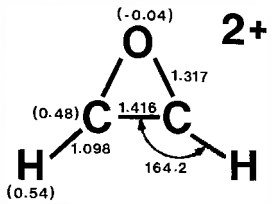
The T value measured at the horn of the dished peak associated with this reaction is 3.6 eV, which corresponds to an intercharge distance of 4 Å. The distance between the two hydrogen atoms in the transition state $\{H{-}C{=}O\cdots H\}^{2\oplus}$ was calculated (6–31G*) to be 4.078 Å[41].

Among the ten minima located on the $C_2H_2O^{2\oplus}$ potential energy surface[44], the ketene dication (**39**) was found to represent the global minimum, followed by the oxirene dication (**40**) which is predicted to be only 27 kcal/mol less stable than **39** (MP2/6–31G*//4–31G + ZPE). For the *neutral* system at the highest level of theory an energy difference between **39** and **40** of ca. 80 kcal/mol was obtained[45], which emphasizes the relative destabilizing effect of the cyclic 4π electron configuration of oxirene. Removal of two electrons diminishes this unfavoured configuration. Although the formations of **39** and **40** are highly unlikely in solution because of favoured disproportionation reactions and the thermochemical instability of the two dications (**39**: ΔH_f° = 651 kcal/mol; **40**: ΔH_f° = 678 kcal/mol), observation in the gas phase is feasible. While charge separation of **39** and **40** are exothermic, large barriers prevent them from spontaneous dissociation. In fact, charge-stripping from ionized ketene results in the formation of a stable dication, and the comparison between the measured ionization energy (18.6 eV) and the one calculated for vertical ionization (18.56 eV) is excellent. Experi-

ments towards identification of **40** were not possible because of the lack of an appropriate stable precursor.



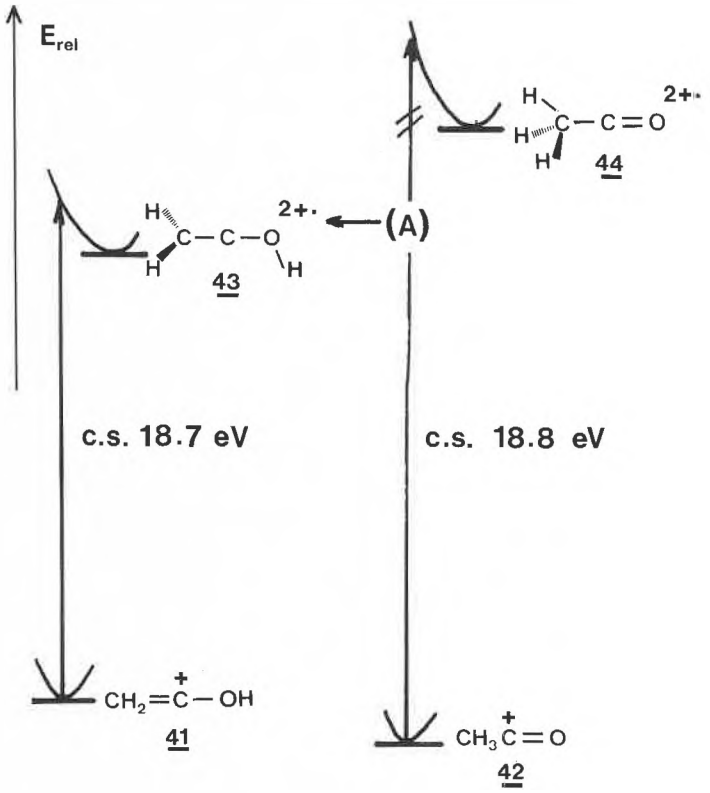
39 (C_{2v})



40 (C_{2v})

The repeatedly noted reversal in stability when comparing isomers of neutral and ionized species holds also for $C_2H_3O^{\oplus}$ and $C_2H_3O^{2\oplus\odot}$ ions. While for the monocation the acetylium ion, $CH_3CO^{\oplus}$ (**42**), represents the global minimum, followed by the 1-hydroxyvinyl cation (**41**), for the $C_2H_3O^{2\oplus\odot}$ species the latter (**43**) is predicted[46] to be the most stable isomer: **44**, the acetyl dication, is found at the MP2/6–31G*//4–31G level of theory to be 29 kcal/mol less stable than **43**. As for all the other dications mentioned in this article, generation of both dications in solution is highly unlikely on the grounds of their tendency to either protonate the solvent shell or to attract an electron or an anion from it. In the gas phase, however, the high barrier should prevent them from dissociating spontaneously. In fact, charge-stripping of **41** results in the formation of **43**[46] with an ionization energy of 18.7 eV, which is in satisfying agreement with the calculated vertical ionization energy of 17.9 eV. Starting from **42** one can also generate a stable $C_2H_3O^{2\oplus}$ species; there is, however, a discrepancy between the measured and the calculated ionization energies (IE_{exp} = 18.8 eV; calculated for IE_v = 22.6 eV and for IE_{ad} = 20.9 eV), which for the time being is not fully resolved. One explanation may be that, like in the charge-stripping of $CH_3X^{\oplus\odot}$, a Rydberg state of $CH_3CO^{\oplus}$ (denoted as (A) in Scheme 2) is involved from which electron ejection is accompanied with or followed by isomerization to **43** (Scheme 2). Further studies aimed at understanding the physics of the charge stripping reactions are highly desirable in order to resolve the discrepancy.

Scheme 2



9. Prospects

Among the topics related to poly-charged cations and which are likely to be discussed in the near future will be the following:

1) As illustrated in the preceding chapters a more detailed understanding of the physics of charge-stripping from organic cations is highly desirable not the least to remove the discrepancies between calculated and measured ionization energies found for some systems. This should also include rigorous theoretical treatments of the dissociation pathways of poly-charged cations which, due to the mixing of polarization states, are all but trivial to perform properly[12d, 47].

2) A thorough spectroscopic characterization – which is now nearly routinely used for many gaseous monocations[48] – is also warranted for multiply-charged cations, and for several small dications promising results were recently published[49].

3) The study of solvated mono-charged cations and anions in the gas phase has provided a deep insight into both intrinsic properties of charged species and the role differential solvation plays[50]. Related gas phase studies on dications are more or less unknown. As the generation in solution of any of the dications discussed in this article is highly unlikely, studies in the gas phase might be feasible, although it must be admitted that the very same processes which prevent the generation of dications in solution (proton transfer to solvent shell or transfer of negatively charged species from it to the dication) may also be operative in the gas phase.

4) The study of neutral and mono-charged van der Waals complexes and clusters with its many facets belongs undoubtedly to the main lines of basic research in chemistry and physics. The recent reports[51] on the successful generation and characterization of multiply-charged cluster ions with up to five (!) elementary charges are extremely encouraging, and more exciting results are likely to emerge in the future.

5) Both experimental and theoretical studies on multiply-charged *small* cations, M^{n+} ($n \geq 3$), will certainly increase in number. There is already compelling evidence[52] for the existence of these truly remarkable species and some of the problems one would like to see solved concern the interplay of binding forces versus Coulomb repulsion, as well as the implications of increasing charge numbers for relative stability orders of isomers, structural modifications, pathways of isomerization and dissociation.

No doubt, the gas phase chemistry and physics of multiply-charged ions will have a bright future.

Since the completion of this review article several papers on multiply-charged ions were published. We note the following ones: «Structure, stability, and energetics of the neutral and singly- and doubly-ionized First- and Second-row hydrides»[53], «Hydroxyacetylen: Erzeugung und Charakter des Neutralmoleküls, Radikalkations und Dikations in der Gasphase»[54], «Ab initio molecular orbital studies on $CH_2O_2^{2\oplus}$-isomers»[55].

Received: September 20, 1985 [FR 20]
Publication delay at author's request.

[1] R.G. Cooks, T. Ast, J.H. Beynon, *Int. J. Mass Spectrom. Ion Phys. 11* (1973) 490; D.L. Kemp, R.G. Cooks, in R.G. Cooks: *Collision Spectroscopy*, Plenum Press, New York (1978) 257; T. Ast, *Adv. Mass Spectrom. 8A* (1980) 555; T. Ast, C.J. Porter, C.J. Proctor, J.H. Beynon, *Bull. Soc. Chem. Beograd 46* (1981) 135; K. Levsen, H. Schwarz, *Mass Spectrom. Rev. 2* (1983) 77.

[2] P. von R. Schleyer, *Am. Chem. Soc. Div. Pet. Chem. Prepr. 28* (1983) 413; for recent reviews on stable carbodications *in solution* see: G.K.S. Prakash, T.N. Rawdah, G.A. Olah, *Angew. Chem. 95* (1983) 356; *Angew. Chem. Int. Ed. Engl. 22* (1983) 390; R.M. Pagni, *Tetrahedron 40* (1984) 4161.

[3] For a comprehensive literature survey with more than 100 references of studies performed over the last decade see: W. Koch, N. Heinrich, D. Stahl, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes 67* (1985) 305.

[4] M. Guilhaus, A.G. Brenton, J.H. Beynon, M. Rabrenovič, P. von R. Schleyer, *J. Phys. B 17* (1984) L605; *J. Chem. Soc. Chem. Commun.* (1985) 210.

[5] K.R. Jennings, *Int. J. Mass Spectrom. Ion Phys. 1* (1965) 127; J. Seibl, *Org. Mass Spectrom. 2* (1969) 1033; J. Appell, J. Durup, F.C. Fehsenfeld, P.G. Fournier, *J. Phys. B7* (1974) 406.

[6] H. Yagisawa, H. Sato, T. Watanabe, *Phys. Rev. A16* (1977) 1352.

[7] J.D. Dunitz, T.K. Ha, *J. Chem. Soc. Chem. Commun.* (1972) 568.

[8] A comprehensive review article on this topic is under preparation: P. von R. Schleyer, H. Schwarz et al.

[9] M. Rabrenovič, C.J. Proctor, T. Ast, C.G. Herbert, A.G. Brenton, J.H. Beynon, *J. Phys. Chem. 87* (1983) 3305.

[10] T. Ast, C.J. Porter, C.J. Proctor, J.H. Beynon, *Chem. Phys. Lett. 78* (1981) 439; C.J. Proctor, C.J. Porter, T. Ast, P.D. Bolton, J.H. Beynon, *Org. Mass Spectrom. 16* (1981) 454; M. Rabrenovič, C.G. Herbert, C.J. Proctor, J.H. Beynon, *Int. J. Mass Spectrom. Ion Phys. 47* (1983) 125; M. Rabrenovič, A.G. Brenton, J.H. Beynon, *ibid. 52* (1983) 175.

[11] D. Stahl, F. Maquin, T. Gäumann, H. Schwarz, P.-A. Carrupt, P. Vogel, *J. Am. Chem. Soc. 107* (1985) 5049.

[12] a) A.W. Hanner, T.F. Moran, *Org. Mass Spectrom 16* (1981) 512; b) P.E.M. Siegbahn, *Chem. Phys. 66* (1982) 443; c) J.A. Pople, B. Tidor, P. von R. Schleyer, *Chem. Phys. Lett. 88* (1982) 533; d) R.W. Wetmore, R.K. Boyd, R.J. LeRoy, *Chem. Phys. 89* (1984) 329.

[13] a) W. Koch, G. Frenking, H. Schwarz, *J. Chem. Soc. Chem. Commun.* (1985) 1119; b) W. Koch, G. Frenking, H. Schwarz, F. Maquin, D. Stahl, *J. Chem. Soc. Perkin Trans. 2*, in press.

[14] C.J. Porter, C.J. Proctor, T. Ast, J.H. Beynon, *Croat. Chem. Acta 54* (1981) 407.

[15] W. Koch, G. Frenking, C.C. Chang, *J. Chem. Phys.*, in press.

[16] C.J. Proctor, C.J. Porter, T. Ast, P.D. Bolton, J.H. Beynon, *Org. Mass Spectrom. 16* (1981) 454.

[17] S.A. Pope, I.H. Hillier, M.F. Guest, J. Kendric, *Chem. Phys. Lett. 95* (1983) 247.

[18] Olah et al., however, have suggested that the proton exchange reactions of $H_3O^{\oplus}$ in solution may proceed via $H_4O^{2\oplus}$: G.A. Olah, G.K.S. Prakash, M. Barzaghi, K. Lammertsma, P. von R. Schleyer, J.A. Pople, *J. Am. Chem. Soc.*, submitted for publication. We thank Prof. Olah and Prof. Schleyer for providing their results prior to publication.

[19] W. Koch, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes 68* (1986) 49.

[20] For reviews see: H. Schwarz, *Nachr. Chem. Tech. Lab. 31* (1983) 451; *Mass Spectrosc. (Tokyo) 32* (1984) 3; L. Radom, W.J. Bouma, R.H. Nobes, B.F. Yates, *Pure Appl. Chem. 56* (1984) 1831.

[21] M.J. Frisch, K. Raghavachari, J.A. Pople, W.J. Bouma, L. Radom, *Chem. Phys. 75* (1983) 323; J.A. Pople, K. Raghavachari, M.J. Frisch, J.S. Binkley, P. von R. Schleyer, *J. Am. Chem. Soc. 105* (1983) 6389; D.A. Dixon, T.H. Dunning, R.A. Eaules, P.O. Gassman, *ibid 105* (1983) 7011.

[22] a) W.J. Bouma, L. Radom, *J. Am. Chem. Soc. 105* (1983) 5484; b) F. Maquin, D. Stahl, A. Sawaryn, P. von R. Schleyer, W. Koch, G. Frenking, H. Schwarz, *J. Chem. Soc. Chem. Commun.* (1984) 504.

[23] For extensive references see: W. Koch, F. Maquin, H. Schwarz, D. Stahl, *J. Am. Chem. Soc. 107* (1985) 2256.

[24] R.H. Nobes, L. Radom, W.R. Rodwell, *Chem. Phys. Lett. 74* (1980) 269.

[25] L.A. Teleshefsky, B.E. Jones, L.E. Abbey, D.E. Bostwick, E.M. Burgers, T.F. Moran, *Org. Mass Spectrom. 17* (1982) 481.

[26] For many references see: a) W. Koch, G. Frenking, H. Schwarz, F. Maquin, D. Stahl, *Int. J. Mass Spectrom. Ion Processes 63* (1985) 59; b) H. Schwarz, *Adv. Mass Spectrom.* (1985), in press.

[27] K. Lammertsma, *J. Am. Chem. Soc. 106* (1984) 4619.

[28] K. Lammertsma, M. Barzaghi, G.A. Olah, J.A. Pople, A.J. Kos, P. von R. Schleyer, *J. Am. Chem. Soc. 105* (1983) 5252.

[29] a) C. Benoit, J.A. Horsley, *Mol. Phys. 30* (1975) 557; b) M. Rabrenovič, J.H. Beynon, *Int. J. Mass Spectrom. Ion Processes 54* (1983) 79.

[30] a) W. Koch, G. Frenking, F. Maquin, D. Stahl, H. Schwarz, *J. Chem. Soc. Chem. Commun.* (1984) 1187; b) G. Frenking, W. Koch, H. Schwarz, *J. Comput. Chem.*, in press.

[31] F. Maquin, D. Stahl, unpublished results.

[32] P. von R. Schleyer, A.J. Kos, J.A. Pople, A.T. Balaban, *J. Am. Chem. Soc. 104* (1982) 3771.

[33] D. Stahl, F. Maquin, *Chimia 37* (1983) 87.

[34] M. Rabrenovič, J.H. Beynon, *J. Chem. Soc. Chem. Commun.* (1983) 1043; *Int. J. Mass Spectrom. Ion Processes 54* (1983) 79; *56* (1984) 85.

[35] S.D. Peyerimhoff, R.J. Buenker, *J. Chem. Phys. 49* (1968) 312; G.A. Olah, M. Simonetta, *J. Am. Chem. Soc. 104* (1982) 330.

[36] C.J. Proctor, C.J. Porter, T. Ast, J.H. Beynon, *Int. J. Mass Spectrom. Ion Phys. 41* (1982) 251.

[37] W. Koch, G. Frenking, *Chem. Phys. Lett. 114* (1985) 178.

[38] T. Drewello, T. Weiske, H. Schwarz, *Angew. Chem. 97* (1985) 855; *Angew. Chem. Int. Ed. Engl. 24* (1985) 869.

[39] C. Guenat, F. Maquin, D. Stahl, W. Koch, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes 63* (1985) 265.

[40] F. Maquin, D. Stahl, H. Schwarz, unpublished results.

[41] W.J. Bouma, L. Radom, *J. Am. Chem. Soc. 105* (1983) 5484.

[42] D. Stahl, F. Maquin, *Chem. Phys. Lett. 106* (1984) 531.

[43] R.G. Cooks, J.H. Beynon, R.M. Caprioli, G.R. Lester: *Metastable Ions*, Elsevier, Amsterdam (1973).

[44] W. Koch, F. Maquin, D. Stahl, H. Schwarz, *J. Chem. Soc. Chem. Commun.* (1984) 1679.

[45] W.J. Bouma, R.H. Nobes, L. Radom, C.E. Woodward, *J. Org. Chem. 47* (1982) 1869.

[46] W. Koch, F. Maquin, H. Schwarz, D. Stahl, *Int. J. Mass Spectrom. Ion Processes 67* (1985) 171.

[47] R.W. Wetmore, R.J. LeRoy, R.K. Boyd, *J. Phys. Chem. 88* (1984) 6318.

[48] T.A. Miller, V.E. Bondybey: *Molecular Ions: Spectroscopy, Structure, and Chemistry*, North-Holland, Amsterdam (1983); M.T. Bowers: *Gas Phase Ion Chemistry*, Vol. *3*: *Ions and Light*, Academic Press, New York (1984).

[49] See for example: P.R. Taylor, *Mol. Phys. 49* (1983) 1297; P.C. Cosby, R. Möller, H. Helm, *Phys. Rev. A28* (1983) 766; D.M. Curtis, J.H.D. Eland, *Int. J. Mass Spectrom. Ion Processes 63* (1985) 241.

[50] P. Ausloos: *Interactions between Ions and Molecules* (NATO Advanced Study Institutes Series B: Physics), Plenum Press, New York (1975); M.T. Bowers: *Gas Phase Ion Chemistry*, Vol. *1* and *2*, Academic Press, New York (1979); M.A. Almoster Ferreira: *Ionic Processes in the Gas Phase* (NATO Advanced Study Institute Series, Vol. 118), D. Reidel, Dordrecht (1984); W.W. Duley, D.A. Williams: *Interstellar Chemistry*, Academic Press, New York (1984).

[51] W. Henkes, G. Isenberg, *Int. J. Mass Spectrom. Ion Phys. 5* (1970) 249; J. Gspann, K. Körting, *J. Chem. Phys. 59* (1973) 4726; O. Echt, K. Sattler, E. Recknagel, *Phys. Lett. A90* (1982) 185; K. Sattler, O. Echt, A. Reyes-Flotte, J. Mühlbach, K. Knapp, P. Pfau, R. Pflaum, P. Höfer, D. Kreisler, E. Recknagel, *Proc. 9th Int. Symp. Molecular Beams*, Freiburg i. Br. (1983) 151; H. Helm, K. Stephan, T.D. Märk, L. Huestis, *J. Chem. Phys. 74* (1981) 3844.

[52] For some references see: W. Henkes, *Z. Naturforsch. A17* (1962) 786; S. Meyerson, R.W. van der Haar, *J. Chem. Phys. 37* (1962) 2458; V.H. Dibeler, F.L. Mohler, R.M. Reese, *ibid. 21* (1953) 180; E.I. Quinn, F.L. Mohler, *J. Res. Natl. Bur. Stand. 62* (1959) 39; F.H. Dorman, J.D. Morrison, *J. Chem. Phys. 35* (1961) 575; A.S. Newton, *ibid. 40* (1964) 607; R.J. Van Brunt, M.E. Wacks, *ibid. 41* (1964) 3195; C.E. Brion, N.L. Paddock, *J. Chem. Soc. A* (1968) 388, 392; F. Figuet-Fayard, J. Chiari, F. Müller, J.P. Ziesel, *J. Chem. Phys. 48* (1968) 478; S. Becker, J.H. Dietze, *Int. J. Mass Spectrom. Ion Phys. 51* (1983) 325; T.D. Märk, *Int. J. Mass Spectrom. Ion Processes 55* (1983) 325; S. Singh, R.K. Boyd, F.M. Harris, J.H. Beynon, *ibid. 66* (1985) 167; W. Koch, H. Schwarz, *Chem. Phys. Lett. 113* (1985) 145.

[53] S.A. Pope, I.H. Hillier, M.F. Guest, *Faraday Symp. Chem. Soc. 19* (1984), paper 8, page 1.

[54] B. v. Baar, T. Weiske, J.K. Terlouw, *Angew. Chem.*, in press.

[55] W. Koch, H. Schwarz, *Chem. Phys. Lett.*, submitted.