Experimental and Theoretical Studies on the Charge Stripping from CH_3X^+ and $CH_2XH^{+\cdot}$ Ions ($X = F, Cl, Br, I, OH, SH,$ or NH_2)

Francis Maquin,[a] Daniel Stahl,*[a] Andrzej Sawaryn,[b] Paul von R. Schleyer,*[b] Wolfram Koch,[c] Gernot Frenking,[c] and Helmut Schwarz*[c]

[a] *Institute de Chimie Physique, École Polytechnique Fédérale, CH-1015 Lausanne, Switzerland*
[b] *Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, D-8520 Erlangen, West Germany*
[c] *Institut für Organische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, West Germany*

Charge stripping from either $CH_2XH^{+\cdot}$ or $CH_3X^{+\cdot}$ cation radicals ($X = F, Cl, Br, I, OH, SH,$ or NH_2) results in the formation of observable dications; a comparison of experimentally derived Q_{min} data for the process $m^+ \rightarrow m^{2+}$ with the computed vertical ionization energies, I.E.$_v$, suggests that whereas electron removal from $CH_2XH^{+\cdot}$ results directly in the formation of the corresponding dications, *i.e.* CH_2XH^{2+}, charge stripping from $CH_3X^{+\cdot}$ does not lead to stable CH_3X^{2+} species, but instead rearrangement (perhaps from a Rydberg state of $CH_3X^{+\cdot}$) is likely to take place to give CH_2XH^{2+} ions.

There has been considerable recent theoretical and experimental interest in the gas phase chemistry of ionized ylides, $CH_2XH^{+\cdot}$, which can also be formally viewed as ion–dipole complexes between $CH_2^{+\cdot}$ and polar molecules XH (X corresponds to a first- or second-row element).[1] The stabilities of $CH_2XH^{+\cdot}$ ions are usually comparable to those of their isomeric forms $CH_3X^{+\cdot}$ (both thermochemically and kinetically). This is in distinct contrast to the behaviour of the neutral parent molecules for which, in general, CH_2XH species do not exist as stable entities;[2] instead, they isomerize *via* 1,2 hydrogen shifts to the substantially more stable CH_3X molecules. Thus, ionization leads to a strong relative stabilization of the unusual structure $CH_2XH^{+\cdot}$. What might happen when a second electron is removed, *i.e.* formation of the dications CH_2XH^{2+} and CH_3X^{2+}, respectively, has been investigated for $X = OH$ with the aid of state-of-the-art *ab initio* molecular orbital calculations.[3] Singlet CH_3OH^{2+} (**1**) is not found to be a stationary point on the potential energy surface; it rearranges spontaneously to a weakly bound complex $H_2\cdot\cdot\cdot\cdot CH{-}OH^{2+}$ (**2**) which dissociates *via* a small barrier of 3 kcal mol^{-1} (1 cal = 4.184 J) into H_2 and $CHOH^{2+}$.[3] In contrast, the dication $CH_2OH_2^{2+}$ (**3**) exists in a deep potential well. The dication (**3**) is calculated to be 74 kcal mol^{-1} more stable than (**2**) and to be prevented from undergoing exothermic dissociation processes owing to high energy barriers.[3] Theoretical results for CH_3OH^{2+} and $CH_2OH_2^{2+}$ were believed[3] to be in agreement with the experimental observations of Holmes *et al.*[4] Charge stripping (C.S.) mass spectrometry[5] experiments gave[4] an intense, narrow peak at *m/z* 16, corresponding to CH_4O^{2+} in the spectrum of $CH_2OH_2^{+\cdot}$ showing that a significant binding energy must indeed exist between $CH_2^{+\cdot}$ and $H_2O^{+\cdot}$. In contrast, the collisional activation mass spectrum of $CH_3OH^{+\cdot}$ does not contain any detectable signal at *m/z* 16,[4] when, for example, helium is used as a collision gas. Similar results were obtained for other $CH_3X^{+\cdot}$ ions and it was concluded[4] that doubly charged ions of the elemental composition CH_3X^{2+} are inaccessible in charge stripping experiments from $CH_3X^{+\cdot}$ precursors. This conclusion, however, is not justified. By using *oxygen* as a collision gas† charge stripping takes place

CH_3OH^{2+}
(**1**)

$H_2\cdot\cdot\cdot\cdot CH{-}OH^{2+}$
(**2**)

$CH_2OH_2^{2+}$
(**3**)

$CH_3OH^{+\cdot}$
(**4**)

$CH_2OH_2^{+\cdot}$
(**5**)

---

† O_2 has been used in numerous other cases as an efficient collision gas for charge stripping processes. *e.g.* D. Stahl and F. Marquin, *Chimia*, 1983, 87.

Table 1. Vertical ionization energies, Q_{min} for the process $m_1{}^{+} \rightarrow m_1{}^{2+}$.[a]

Precursor	Q_{min}/eV	Q_{min}/eV	Precursor
$CH_2OH_2{}^{+\cdot}$ (**5**)	16.50 ± 0.04	16.34 ± 0.05	$CH_3OH^{+\cdot}$ (**4**)
$CH_2SH_2{}^{+\cdot}$	19.78 ± 0.05	20.18 ± 0.04	$CH_3SH^{+\cdot}$
$CH_2NH_3{}^{+\cdot}$	18.85 ± 0.06	17.69 ± 0.07	$CH_3NH_2{}^{+\cdot}$
$CH_2FH^{+\cdot}$	17.92 ± 0.03	17.23 ± 0.07	$CH_3F^{+\cdot}$
$CH_2ClH^{+\cdot}$	17.47 ± 0.04	18.16 ± 0.03	$CH_3Cl^{+\cdot}$
$CH_2BrH^{+\cdot}$	17.62 ± 0.03	17.91 ± 0.07	$CH_3Br^{+\cdot}$
$CH_2IH^{+\cdot}$	16.30 ± 0.04	17.94 ± 0.05	$CH_3I^{+\cdot}$
$CHClClH^{+\cdot}$	16.12 ± 0.02	16.23 ± 0.03	$CH_2Cl_2{}^{+\cdot}$

[a] The Q_{min}-values represent the average of 10—20 individual measurements, and the errors are given as $S/n^{1/2}$.

and signals for stable dications are observed starting from either $CH_2XH^{+\cdot}$ or $CH_3X^{+\cdot}$ precursors;‡ the energies needed to remove one electron from monocations are given in Table 1 [denoted as Q_{min} = I.E.(m^+)−I.E.(m) (I.E. = Ionization Energy)].

For the isomeric pair $CH_3X^{+\cdot}/CH_2XH^{+\cdot}$ (X = OH and F) we have compared the experimentally derived Q_{min}-values, for generating dications, with those calculated by *ab initio* MO-calculations using GAUSSIAN 76,[6a] extended by a Møller–Plesset perturbation calculation[6b,c] terminated at second order to account for the correlation energy. Energy calculations were performed at MP2/6-31G* level, with geometries optimized at MP2/6-31G* (X = F)[6d] and 6-31G* (X = O),[6e] respectively. For the vertical ionization of $CH_2OH_2{}^{+\cdot}$ an ionization energy, I.E.$_v$, of 16.60 eV has been calculated; this value is in excellent agreement with the experimentally determined Q_{min} = 16.50 eV. Geometric relaxation of the so-obtained $CH_2OH_2{}^{2+}$ ion results in a species (**3**), the electronic and geometric details of which have already been discussed in detail by Bouma and Radom.[3] Less straightforward is the interpretation for the process of removing a single electron from ionized methanol (**4**). The experimental value of Q_{min} = 16.34 eV is by no means matched by the one calculated for the vertical ionization of $CH_3OH^{+\cdot}$ (I.E. = 22.05 eV). It is highly unlikely that the huge discrepancy of 5.7 eV is due to large errors in either the computational method§ or the experiments. Instead, we believe that removal of an electron from $CH_3OH^{+\cdot}$ (**4**) does not result in the formation of an (unstable)[3] methanol dication, CH_3OH^{2+} (**1**), but is accompanied by hydrogen rearrangement to give eventually the stable methyleneoxonium dication $CH_2OH_2{}^{2+}$ (**3**). In line with this interpretation is the fact that the Q_{min}-value for ionizing $CH_3OH^{+\cdot}$ (**4**) is 0.16 eV lower than that for $CH_2OH_2{}^{+\cdot}$ (**5**), which is a consequence of the fact that (**5**) is thermochemically more stable by 0.3 eV[4] than (**4**). At what stage does the isomerization $CH_3OH^{+\cdot} \rightarrow CH_2OH_2{}^{2+}$ occur? If the isomerization were to involve the molecular ion of $CH_3OH^{+\cdot}$, *i.e.* $CH_3OH^{+\cdot} \rightarrow CH_2OH_2{}^{+\cdot}$, following by charge stripping of the excited methyleneoxonium ion, simple thermochemical considerations show that owing to the high barrier[3,4,7] of this rearrangement and the fact that one is dealing with an isolated species, Q_{min} for $CH_3OH^{+\cdot}$ should be as low as 14.9 eV. This again is in disagreement with the experimental value. Moreover, as CH_3OH^{2+} is not directly accessible energetically, we suggest that collision of $CH_3OH^{+\cdot}$ with oxygen molecules leads initially to a Rydberg state of $CH_3OH^{+\cdot}$ (A in Figure 1) from which an electron is ejected, followed (or accompanied) by hydrogen rearrangement to give eventually the stable $CH_2OH_2{}^{2+}$ species (**3**).

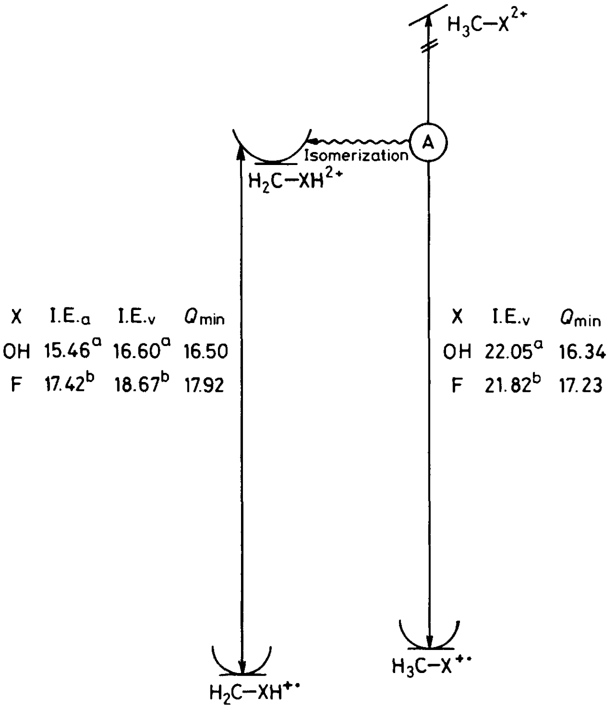

Figure 1. Relative energies (eV) for removal of one electron from $CH_2XH^{+\cdot}$ and $CH_3X^{+\cdot}$ ions. Vertical ionization energies (I.E.$_v$) and adiabatic energies (I.E.$_a$) were obtained by either (a) MP2/6-31G*//6-31G* or (b) MP2/6-31G*//MP2/6-31G* calculations. Q_{min} data were determined in charge stripping experiments.

Similar results were obtained for the fluorine derivatives $CH_3F^{+\cdot}$ *versus* $CH_2FH^{+\cdot}$ (Figure 1). The calculated vertical ionization energies of $CH_2FH^{+\cdot}$ ions are in reasonable agreement with the Q_{min}-data, whereas those for $CH_3F^{+\cdot}$ precursor ions differ by as much as 4.6 eV.

We conclude that (i) charge stripping from $CH_3X^{+\cdot}$ ions is possible provided a suitable collision gas is used and (ii) removal of the electron for $CH_3X^{+\cdot}$ is not a process leading to the formation of CH_3X^{2+} dications but is very likely to be associated with hydrogen rearrangement, thus generating eventually the stable methyleneoxonium dications CH_2XH^{2+}. The latter species are directly accessible by charge stripping from $CH_2XH^{+\cdot}$.

---

‡ Experimental conditions: $CH_2XH^{+\cdot}$ ions are generated *via* dissociative ionization (70 eV ionizing energy) of suitable precursors (*e.g.*, $HOCH_2–CH_2XH \rightarrow HOCH_2–CH_2XH^{+\cdot} \rightarrow CH_2O + CH_2XH_2{}^{+\cdot}$), and $CH_3X^{+\cdot}$ by direct ionization of neutral CH_3X in a VG analytical ZAB-2F mass spectrometer. The ions of interest are accelerated by a potential of 8 kV before being separated by the magnetic sector. The collision gas used was O_2 at a pressure of *ca.* 10^{-4} Torr. The products of the collision-induced reactions were studied by scanning the electrostatic analyser. Q_{min} was determined from the positions of the relevant peaks in the ion kinetic energy spectrum, and the value of Q_{min} = 15.7 eV for the process $C_7H_8{}^{+} \rightarrow C_7H_8{}^{2+}$ in toluene was used as a standard to calibrate the energy scale in all measurements (F. H. Dorman and J. D. Morrison, *J. Chem. Phys.*, 1961, **35**, 575).

§ It should also be mentioned that, by applying Koopman's theorem (T. Koopman, *Physica*, 1933, **1**, 104) the calculated energy needed to remove an electron vertically from the SOMO of $CH_3OH^{+\cdot}$ is as much as 6.5 eV higher (6-31G*//6-31G*) than the one determined experimentally. Similarly, it was calculated (6-31G*//6-31G*) that vertical ionization of $CH_3F^{+\cdot}$ would require energies which are also substantially larger (by *ca.* 6.5 eV) than those obtained by charge stripping.

Financial support of our work by the Fonds National Suisse pour la Recherche Scientifique, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Gesellschaft von Freunden der Technischen Universität Berlin (T.U.B.) is gratefully acknowledged. We are particularly indebted to the Computer Centre, T.U.B., for the generous supply of computer time.

Received, 23rd January 1984; Com. 089

References

1 For reviews see H. Schwarz, *Nachr. Chem. Tech. Lab.*, 1983, **31**, 451; H. Schwarz, *J. Mass Spectroscopy*, in the press.

2 For leading references see: M. J. Frisch, K. Raghavachari, J. A. Pople, W. J. Bouma, and L. Radom, *Chem. Phys.*, 1983, **75**, 323; J. A. Pople, K. Raghavachari, M. J. Frisch, J. S. Binkley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1983, **105**, 6389; D. A. Dixon, T. H. Dunning, R. A. Eaules, and P. O. Gassman, *ibid.*, p. 7011 .

3 W. J. Bouma and L. Radom, *J. Am. Chem. Soc.*, 1983, **105**, 5484.

4 J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *J. Am. Chem. Soc.*, 1982, **104**, 2931; J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *Can. J. Chem.*, 1983, **61**, 2305.

5 K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, 1965, **1**, 227; J. Seibl, *Org. Mass Spectrom.*, 1969, **2**, 1033; R. G. Cooks, J. H. Beynon, and T. Ast, *J. Am. Chem. Soc.*, 1972, **94**, 1004; T. Ast, C. J. Porter, C. J. Procter and J. H. Beynon, *Bull. Soc. Chim. Beograd.*, 1981, **46**, 135; R. P. Morgan, J. H. Beynon, R. H. Bateman, and B. N. Green, *Int. J. Mass Spectrom. Ion Phys.*, 1978, **28**, 171; K. Levsen and H. Schwarz, *Mass Spectrom. Rev.*, 1983, 77.

6 (a) J. S. Binkley, R. A. Whitesides, R. H. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, Quantum Chemistry Program Exchange. No. 368; (b) C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618; (c) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.*, 1976, **10**, 1; (d) W. J. Bouma, B. F. Yates, and L. Radom, *Chem. Phys. Lett.*, 1982, **92**, 620; (e) R. A. Whitesides, M. J. Frisch, J. S. Binkley, D. J. De Frees, H. B. Schlegel, K. Raghavachari, and J. A. Pople, 'Carnegie-Mellon Quantum Chemistry Archive,' Pittsburgh, USA, 1981.

7 W. J. Bouma, R. H. Nobes, and L. Radom, *J. Am. Chem. Soc.*, 1982, **104**, 2929; W. J. Bouma, J. K. MacLeod, and L. Radom, *ibid.*, p. 2930.