The Formation in the Gas Phase of $HO{-}C{\equiv}C{-}OH$, $H_2N{-}C{\equiv}C{-}NH_2$, $H_2N{-}C{\equiv}C{-}OH$, and Related Compounds by Selective Reduction of their Cations**

Johan K. Terlouw*, Peter C. Burgers*, Ben L.M. van Baar, Thomas Weiske, and Helmut Schwarz*

Dedicated to Professor Ferdinand Bohlmann on the occasion of his 65th birthday

Abstract: The novel molecules $XC{\equiv}CY$ where X and Y are OH, NH_2, and OCH_3, as well as hydroxy- and aminoketene, have been prepared and identified in the gas phase by neutralization-reionization mass spectrometry. It is concluded that these molecules reside in deep potential wells.

This paper forms part of the work in progress in various laboratories with the aim of synthesizing unconventional small solitary molecules via reduction of their ionic counterparts[1-6]. The subject is gaining in coherence and may be called the chemistry of unusual molecules. At the beginning of our report on the generation of the hitherto unknown title compounds an appropriate background should be sketched out.

The apparatus used is a mass spectrometer whose place in the laboratory as an analytical tool and research instrument is now well established. With this machine a beam of electrons causes gas phase molecules to lose an electron. If the energy transfer upon electron impact is sufficiently large the parent ion may dissociate into, it is hoped, structure characteristic fragments. The ions reside in the ion source for approximately 10^{-6} s, are then accelerated to about 10 keV, and the mass spectrum is obtained by varying the magnetic field strengh[7]. Over the past decade it has become clear that within the above 10^{-6} s organic cations may undergo more or less complex rearrangement reactions, whereby via a molecular elimination a product ion is formed whose corresponding neutral molecule is often not known to exist[8]. That such rearrangement reactions do take effect is explained by the Quasi-Equilibrium-Theory (QET)[9]. For example, propynoic acid, $HC{\equiv}C{-}CO_2H$, after ionization, eliminates CO as exemplified by the presence of an intense peak at *m/z* 42, $C_2H_2O^{\oplus\odot}$, in its mass spectrum[10]. With a double-focussing mass spectrometer of BE geometry (magnet (B) followed by electric analyzer (E)) the structure of these daughter ions can be determined as follows: The daughter ions are after acceleration selectively transmitted through the electromagnet and are then submitted to collision with an inert gas (for example helium), leading to secondary product ions which are recorded by adjusting the strength of the electric field. The collisional activation (CA)[11] mass spectrum thus obtained (which can be regarded as a mass spectrum of a mass selected ion (MS/MS)[12] reflects the structure of the daughter ion. Using this technique it was shown[10] that extrusion of CO from ionized propynoic acid leads to $HC{\equiv}C{-}OH^{\oplus\odot}$ (and *not* ionized ketene), most probably via a 1,3-hydroxyl migration[13]. It is not within the context of this paper to list all the novel ions generated in the gas phase but it will suffice to say that many unconventional ions, such as the above and also ylide[8] and distonic ions[14] can be readily obtained by dissociative ionization[8]. This fact has inspired various research groups *to devise experiments whereby the novel ion is neutralized by charge-exchange in hopes to generate unusual molecules which are otherwise not accessible*[1-6].

The generation and identification of such neutral species is achieved by a double collision experiment[6]. The set-up consists of a mass spectrometer of BE type which contains amidst the two sectors a tandem collision cell with an ion beam deflector between the individual chambers. A reducing agent (metal vapour or nobel gas) is admitted to the first chamber to neutralize the cations ($M^{\oplus}$) by electron transfer to generate neutral M having the same momentum as $M^{\oplus}$. The unreacted ions are then deflected by the beam deflector and thus only neutrals M continue their flight and enter the second chamber wherein they are ionized by collision with a suitable oxidizing agent. This oxidation step must be sufficiently violent to produce not only stable ions $M^{\oplus}$, but also excited ions which then fragment thus providing structure-diagnostic informations. The ions are then recorded by scanning the electric field strength. Ionization of the neutral, followed by dissociation, can be achieved by collision with He or O_2[3-6,15] (in the following He is used). For the reduction step opinions differ as to what the most suitable reducing agent is[5,16]. *McLafferty* and coworkers[16] argue that metal vapour gives the best result but we have demonstrated[4] that xenon is a good electron transfer agent and moreover is easy to manipulate. In the following experiments neutralization is performed with Xe and reionization is achieved with He. The above described technique has been referred to as *neutralization-reionization mass spectrometry* (NRMS) by *Danis* et al.[3] and is a promising, powerful technique for the synthesis of unconventional molecules, including hypervalent molecules[17]. For example, electron transfer from xenon to $HC{\equiv}C{-}OH^{\oplus\odot}$ leads to neutral hydroxyacetylene[10] which retains its structure as evidenced by its unique NR mass spectrum

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**Correspondence:*
Dr. J.K. Terlouw
Analytical Chemistry Laboratory,
University of Utrecht
Croesestraat 77A, NL-3522 AD Utrecht
(The Netherlands)
Prof. Dr. P.C. Burgers
Département de Chimie, Université Laval
Quebec, GIK 7P4 (Canada)
Prof. Dr. H. Schwarz
Institut für Organische Chemie
der Technischen Universität Berlin
Strasse des 17. Juni 135, D-1000 Berlin 12

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and is thus a species which lies in a deep potential well.

All following experiments were performed using a Vacuum Generators ZAB-2F mass spectrometer[18] equipped with a tandem collision cell and beam deflector[4–6].

A neutralization-reionization experiment consists of three steps: (1) A precursor ion P is sought which upon dissociative ionization could conceivably yield the ionic form of the desired molecule M, i.e. $P^{\oplus\odot} \rightarrow M^{\oplus\odot} + F$. (2) The structure of $M^{\oplus\odot}$ is determined by collisional activation[11] and, if necessary, by other complementary techniques such as metastable ion and appearance energy measurements[19]. (3) $M^{\oplus\odot}$ is neutralized by collision with xenon and only the neutral species are allowed to enter the second collision cell; the collisionally induced dissociative ionization of the neutrals, caused by collision with helium, leads to a NR mass spectrum which may be compared with reference CA mass spectra ($M^{\oplus\odot} \rightarrow M \rightarrow M^{\oplus\odot} \rightarrow F_1^{\oplus}$, $F_2^{\oplus}$, etc.). Note that if M is a stable species a reasonably intense signal corresponding to $M^{\oplus\odot}$ must be present in the NR mass spectrum.

Inspired by our previously reported gas phase synthesis of hydroxy-[10] and amino-acetylenes[20] we set out to produce the hitherto unknown disubstituted acetylenes HO−C≡C−OH and H_2N−C≡C−NH_2, as well as the mixed analogue H_2N−C≡C−OH. We now shall discuss these examples step by step.

HO−C≡C−OH

Step (1): It is known from the literature[21] that commercially available squaric acid reveals an intense peak at *m/z* 58 ($C_2H_2O_2$) in its electron impact (EI) mass spectrum (Scheme 1).

Scheme 1

Step (2): The structure of these $C_2H_2O_2^{\oplus\odot}$ ions was determined by collisional activation mass spectrometry. It was observed that upon collision, as well as unimolecularly, these ions predominantly fragment to produce an ion at *m/z* 29. Two isomeric [H, C, O]$^{\oplus}$ ions exist, namely $HCO^{\oplus}$ and $COH^{\oplus}$[22]. The structure of the *m/z* 29 daughter ions was determinded by an experiment in which ions formed unimolecularly or by collision in the first drift region, are selectively transmitted through the electromagnet and subsequently structurally analyzed by collisional activation in the second drift region. It was evident from the resulting CA mass spectrum that these *m/z* 29 ions are $COH^{\oplus}$ only and *not* $HCO^{\oplus}$. This observation immediately rules out that the precursor is ionized glyoxal, H(O)C−C(O)$H^{\oplus\odot}$, as this ion generates $HCO^{\oplus}$. In addition, ionized glyoxal also abundantly forms $H_2CO^{\oplus\odot}$ by loss of CO, a reaction which the $C_2H_2O_2^{\oplus\odot}$ ions generated from squaric acid do not undergo at all. This reaction will be discussed in detail elsewhere but it will suffice to say that we have good evidence that it proceeds via the stable hydrogen-bridged species O=C(H)· ·H· · ·C=$O^{\oplus\odot}$. Also, hydroxyketene molecular ions HO−C(H)=C=$O^{\oplus\odot}$ (produced by C_2H_4 loss from ionized 2-hydroxycyclobutanone or by successive losses of CO_2 and H_2O from ionized tartronic acid) and $^{\odot}CH_2$−O−C=$O^{\oplus}$ (from ethylene carbonate) can be discarded as candidates because these species also, and perhaps not surprisingly, cleave off CO to produce *m/z* 30 ($CH_2O^{\oplus\odot}$). Hence, we conclude that the $C_2H_2O_2^{\oplus\odot}$ ions generated from ionized squaric acid have the structure HO−C≡C−$OH^{\oplus\odot}$ (we note in passing that *m/z* 29, *pure* $COH^{\oplus}$, forms the base peak in the mass spectrum of squaric acid and thus the latter molecule is a good source of $COH^{\oplus}$, much better than the molecule used hitherto, i.e $CD_3OH^{\oplus\odot} \rightarrow COH^{\oplus} + D_2 + D^{\odot}$)[22a, b].

Step (3): The NR mass spectrum of HO−C≡C−$OH^{\oplus\odot}$ was recorded as described above and is shown in Fig. 1, together with the CA mass spectrum of HO−C≡C−$OH^{\oplus\odot}$. It can be seen that a significant fraction of the species survives the redox reactions and therefore neutral $C_2H_2O_2$ must represent a stable molecule. Also *m/z* 30 is absent in the NR mass spectrum so that the neutral species cannot have rearranged to glyoxal or hydroxyketene because these neutrals abundantly generate upon reionization *m/z* 30 (see above). Hence, we conclude that the surviving neutrals are HO−C≡C−OH and in order for them to survice the reduction step they must reside in a deep potential well. The NR mass spectrum of HO−C≡C−$OH^{\oplus\odot}$ contains an intense peak at *m/z* 28 (see Fig. 1b) corresponding to $CO^{\oplus\odot}$. Its origin is a follows[5]: The distance between the magnet and neutralization cell is approximately 1 m and so the mass selected ion may decompose unimolecularly (metastable ions) in this region. Now, the sole unimolecular fragmentation of HO−C≡C−$OH^{\oplus\odot}$ is the C-C bond cleavage reaction yielding $COH^{\oplus}$ with the corresponding neutral fragments, i.e. $HCO^{\odot}$, $COH^{\odot}$ or $H^{\odot}$+CO. (We have indirect evidence that the neutral actually is the long-sought COH radical and are persuing its definitive unequivocal identification). These neutrals too will be transmitted to the ionization cell leading to ions which contribute to the NR mass spectrum[5]. We observed that neutral $HCO^{\odot}$ and $COH^{\odot}$, prepared by neutralization of $HCO^{\oplus}$ and $COH^{\oplus}$, predominantly produce CO upon reionization (*m/z* 29 : *m/z* 28 ≈ 10:100) and so we conclude that the intense signal at *m/z* 28 in the NR mass spectrum chiefly is due to (dissociative) ionization of metastably generated neutrals.

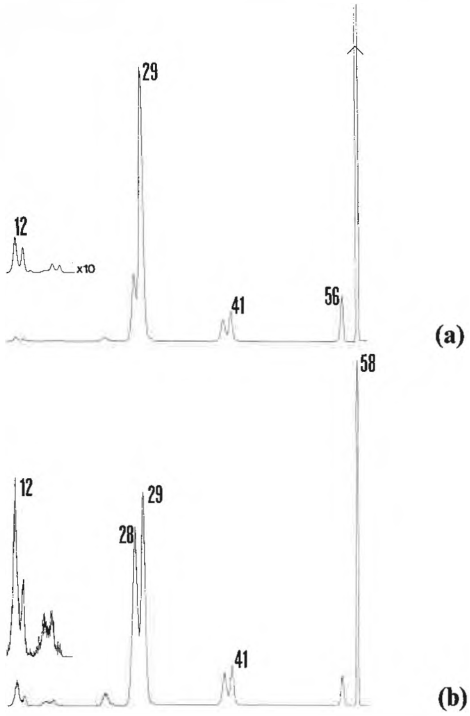
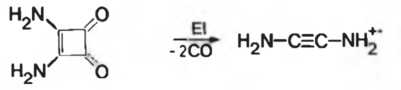


Fig. 1. Collisional activation (CA) mass spectrum (a) and neutralization-reionization (NR) mass spectrum (b) of HO−C≡C−OH$^{\oplus\odot}$.

H_2N−C≡C−NH_2

It was observed that the bisamide of squaric acid[23] too upon electron impact ionization loses two CO molecules to generate H_2N−C≡C−$NH_2^{\oplus\odot}$ (Scheme 2).

Scheme 2



Those daughter ions may undergo a rearrangement/dissociation reaction, leading to $HCNH_2^{\oplus\odot}$ and CNH (also a minor process leading to $HCNH^{\oplus\odot}$ takes effect). Because this reaction proceedes so abundantly the CNH molecules are expected to contribute significantly to the NR mass spectrum of H_2N−C≡C−$NH_2^{\oplus\odot}$. Indeed the spectrum (Fig. 2b) conforms to this expectation: Intense signals are present at *m/z* 27 ($CNH^{\oplus\odot}$) and *m/z* 26 ($CN^{\oplus}$, loss of $H^{\odot}$ from $CNH^{\oplus\odot}$). Note, however, that the neutralized H_2N−C≡C−NH_2 species preferentially forms upon dissociative ionization *m/z* 28, formally $CNH_2^{\oplus}$, a highly structure characteristic reaction. Also peaks corresponding to $NH_2^{\odot}$ loss and successive $H^{\odot}$ atom losses are clearly present. Equally important is the observation that *m/z* 29 ($HCNH_2^{\oplus\odot}$) is only a minor peak in the NR mass spectrum. This peak obviously is the result of a rearrangement reaction taking place within the ionic species. Because the fragmenting ions have only very short lifetimes after reionization (at most 0.2 μs[6]), time consuming rearrangement processes will be suppressed compared to the long-lived (about 10 μs) ions sampled by collisional activation. Hence, all the above results show that $H_2N-C{\equiv}C-NH_2$ is a stable species too.

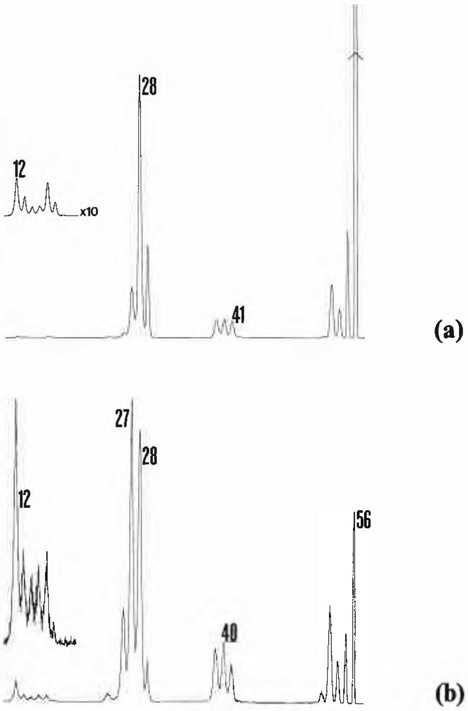
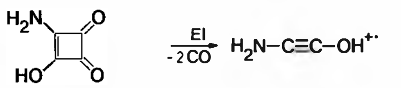


Fig. 2. CA mass spectrum (a) and NR mass spectrum (b) of $H_2N-C{\equiv}C-NH_2^{\oplus\ominus}$.

$H_2N-C{\equiv}C-OH$

The monoamide of squaric acid also eliminates upon dissociative ionization two CO molecules (Scheme 3) to produce $C_2H_3NO^{\oplus\ominus}$ ions.

Scheme 3



The CA mass spectrum of these ions is shown in Fig. 3a and is quite distinct from that of the isomeric aminoketene (generated by loss of H_2O from ionized glycine enol, $H(NH_2)C{=}C(OH)_2^{\oplus\ominus}$[24]). The CA mass spectrum of $H_2N-C{\equiv}C-OH^{\oplus\ominus}$ is dominated by m/z 28, $[H_2, N, C]^{\oplus}$. Only few of the $H_2N-C{\equiv}C-OH^{\oplus\ominus}$ ions are metastable and thus the amount of contamination of the NR mass spectrum by metastably generated neutrals will be small. The NR mass spectrum, shown in Fig. 3b, confirms this expectation. It can be seen that the NR mass spectrum of $H_2N-C{\equiv}C-OH^{\oplus\ominus}$ is close to the CA mass spectrum. For this reason we conclude that the molecule $H_2N-C{\equiv}C-OH$ is a stable species too.

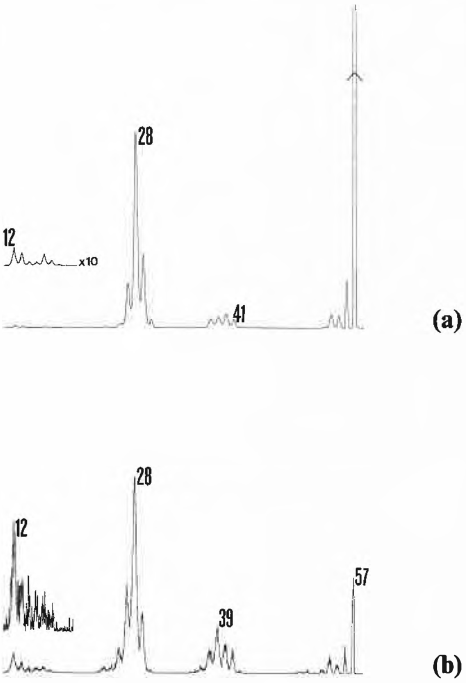


Fig. 3. CA mass spectrum (a) and NR mass spectrum (b) of $H_2N-C{\equiv}C-OH^{\oplus\ominus}$.

So far we have shown that the molecules $X-C{\equiv}C-Y$ (X, Y = OH, NH_2) can be made in the gas phase. Using the same technique we have also produced other interesting molecules, such as $CH_3O-C{\equiv}C-X$ (X = OCH_3, OH, NH_2) as well as neutral hydroxy- and aminoketene. It is again mentioned that in all cases a significant fraction of the ions survive the two collision events and hence all the above neutral molecules reside in deep potential wells. Note that the corresponding ions are interesting in themselves, because they fragment to produce often long-sought small organic cations. Thus $CH_3OC{\equiv}COCH_3^{\oplus\ominus}$ produces in high yield $CH_3-O^{\oplus}{=}C$[25] and not the well-known $CH_3-C^{\oplus}{=}O$ isomer; $H_2NC{\equiv}COCH_3^{\oplus\ominus}$ loses $CH_3^{\ominus}$ and CO to produce $CNH_2^{\oplus}$, which is of potential interest in interstellar chemistry[26], and, finally, $HOC{\equiv}COH^{\oplus\ominus}$ forms $COH^{\oplus}$. Attempts are being made to neutralize these species and to unequivocally determine the structure of the surviving neutrals.

In conclusion, elusive molecules of the type $X-C{\equiv}C-Y$ (X, Y = OH, NH_2, and OCH_3) can be made by neutralization of their corresponding cation radicals in the gas phase. We are convinced that many other fascinating small neutrals, which are inaccessible in solution because of solvent-induced rearrangements[27] can be conveniently made in the gas phase and characterized by the powerful method of neutralization-reionization mass spectrometry.

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