Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 249–250 (2006) 311–316

www.elsevier.com/locate/ijms

A novel route to $H_2O_2^{+\bullet}$ ions via direct generation of the oxywater cation $H_2OO^{+\bullet}$

Giulia de Petris*, Antonella Cartoni, Romano Cipollini, Anna Troiani

Dipartimento di Studi di Chimica e Tecnologia delle, Sostanze Biologicamente Attive, Università "La Sapienza", P.le Aldo Moro 5, Roma 00185, Italy

Received 25 October 2005; received in revised form 13 December 2005; accepted 13 December 2005

Abstract

The oxywater cation $H_2OO^{+\bullet}$ was generated in the gas phase by ionization of mixtures containing O_3, O_2 and H_2O. Different ionic mixtures, rich in either the $H_2OO^{+\bullet}$ or the $HOOH^{+\bullet}$ isomer, were obtained by $O_3/O_2/H_2O–O_2/H_2O$ CI, and by $CH_3OH/O_2–CH_2O/O_2$ CI, respectively. The $H_2O_2^{+\bullet}$ ions were characterized by high-resolution CAD mass spectrometry, and structural and energetic effects were examined.

Keywords: Mass spectrometry; Distonic ions; Oxywater cation; Ozone chemistry

---

1. Introduction

The $H_2O_2^{+\bullet}$ ion is an example of radical cation whose conventional structure, $HOOH^{+\bullet}$, is more stable than the distonic form, $H_2OO^{+\bullet}$ [1,2]. Much of the interest devoted to the deceptively simple $H_2O_2^{+\bullet}$ system [3–6] reflects the relevance to the chemistry of distonic ions, often more stable than their conventional isomers [1,2,7]. High-level CCSD and DFT calculations predicted that the oxywater cation $H_2OO^{+\bullet}$ lies 23 kcal mol^{-1} higher in energy than $HOOH^{+\bullet}$, and resides in a rather deep well, characterized by sizable barriers to the isomerization and dissociation [3–6]. A comparison with the neutral H_2OO, loosely bound and far higher in energy than HOOH, shows that the ionization considerably stabilizes the oxywater structure, even though it does not affect the stability order [3,4]. The stability is instead reversed on the quartet surface of $H_2O_2^{+\bullet}$, where the oxywater cation is more stable than the $HOOH^{+\bullet}$ isomer [6].

Due to the viable [1,2] hydrogen shift, obtaining pure populations of $H_2OO^{+\bullet}$ ions is a quite difficult task, yet neither is the analysis of $HOOH^{+\bullet}$ free from complications. Nonetheless, no reaction has ever been investigated that accesses the $H_2O_2^{+\bullet}$ potential energy surface by generation of $H_2OO^{+\bullet}$.

We here report a novel route to $H_2O_2^{+\bullet}$ ions, allowing direct formation in the gas phase of the oxywater cation $H_2OO^{+\bullet}$. The process, related to ozone ion chemistry, contributes to elucidate the ozone reactivity leading to hydrogen peroxide structures, potentially relevant to the atmospheric odd hydrogen content [8]. Structural and energetic effects involved in the mass spectrometric study of $H_2O_2^{+\bullet}$ ions are also examined in mixtures rich in either $HOOH^{+\bullet}$ or $H_2OO^{+\bullet}$ ions.

2. Experimental

2.1. CI–CAD experiments

The experiments were performed using a modified ZABSpec oa-TOF instrument (VG Micromass) of EBE-TOF configuration, where E, B stand for electric and magnetic sectors and TOF for orthogonal time-of-flight mass spectrometer. The instrument was fitted with an EI (electron impact)/ CI (chemical ionization) source, a gas cell located in the first field free region, and two pairs of cells located after the magnet and in the TOF sector, respectively. Typical operating conditions were as follows: accelerating voltage, 8 keV; source temperature, 433 K; repeller voltage, 0 V; emission current, 1 mA; nominal electron energy, 50 eV. The experiments were performed in the pressure range $0.02 \geq P < 0.3$ Torr, as read inside the source block by a Magnehelic differential pressure gauge. All gases were introduced by separate inlets. Water was introduced by injection of 2 µl into a heated septum inlet ($T = 323$ K), and kept constant during the experiments performed at variable pressure. High-resolution

---

* Corresponding author. Tel.: +39 0649913097; fax: +39 0649913602.
E-mail address: giulia.depetris@uniroma1.it (G. de Petris).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.12.010

mass spectra were recorded in the 7000–12 000 FWHM range. The CAD (collisionally activated dissociation) spectra were recorded in the TOF sector of the instrument at 800 eV collision energy, after mass- and energy-selection of the ion of interest in the third region of the instrument. Argon and He were utilized as collision gases, at 85% trasmittance. After introduction of the collision gas, typical indicated manifold pressures were 6×10^{-7} Torr (He) and 1×10^{-6} Torr (Ar). The spectra were averaged over 100–150 acquisitions, and repeated over an extended time period, under all the employed experimental conditions.

All gases and chemicals were research-grade products from commercial sources, with a stated purity in excess of 99.99% and were used without further purification. Formaldehyde was obtained by depolymerization (by heating to 353–373 K) of paraformaldehyde (Aldrich). $^{18}O_2$ (95% ^{18}O atoms) from CIL and $H_2{}^{18}O$ (97% ^{18}O atoms) from Isotec were utilized. Ozone was prepared by passing UHP grade oxygen (Matheson 99.95 mol%) through a commercial ozonizer, collected in a silica trap cooled at the temperature of 77 K and released by controlled warming of the trap.

2.2. TQMS (tandem quadrupole mass spectrometry) experiments

The experiments were performed using a Waters Quattro Micro Tandem GC–MS/MS equipped with a cool chemical ionization source. The $O_3{}^{+\bullet}$ ions were generated by CI of O_3/O_2 ($P = 2 \times 10^{-5}$ Torr), and $CH_2O^{+\bullet}$ ions were generated by EI of CH_3OH ($P = 4 \times 10^{-6}$ Torr) and CH_2O ($P = 10^{-5}$ Torr). The reactant ions were mass-selected by the first quadrupole (Q1) and driven to the second quadrupole (Q2), a RF-only hexapole, containing the neutral gas at pressures ranging from 8×10^{-5} to 1×10^{-3} Torr. The ion–molecule reactions were investigated at nominal collision energies of 0 eV and the charged products were analyzed by the third quadrupole (Q3).

3. Results and discussion

3.1. $H_2O_2{}^{+\bullet}$ ions in ionized $O_3/O_2/H_2O$ mixtures

High-resolution mass spectra of $O_3/O_2/H_2O$ mixtures were recorded by a multisector mass spectrometer, under chemical ionization (CI) conditions. Two peaks at *m/z* 34 were observed, and assigned by accurate mass measurements to the $^{16}O^{18}O^{+\bullet}$ (the naturally occurring isotopomer of O_2) and $H_2O_2{}^{+\bullet}$ ions, respectively (Fig. 1a). Their ratio varies from 1/5 to 2/1 as the pressure increases.

The $H_2O_2{}^{+\bullet}$ ions are likely generated by the following reaction of the $O_3{}^{+\bullet}$ cation, which gives a number of oxygenated ions by reaction with neutral molecules [9]. No $[O_3–H_2O]^{+\bullet}$ adduct was observed even at the highest investigated pressures, suggesting a direct exothermic reaction:

$$O_3{}^{+\bullet} + H_2O \rightarrow H_2O_2{}^{+\bullet} + O_2 \qquad (1)$$

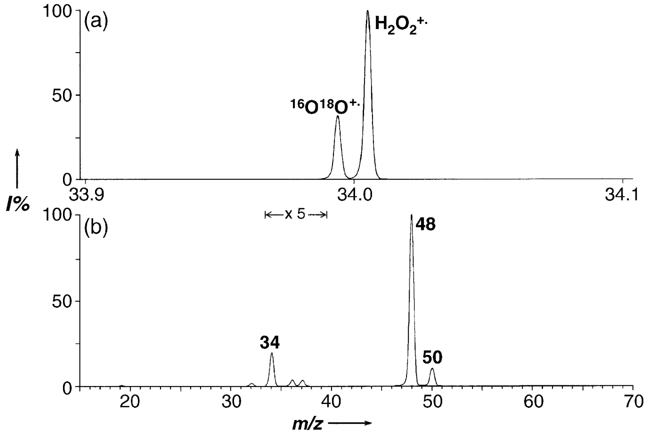

Fig. 1. (a) $^{16}O^{18}O^{+\bullet}$ and $H_2O_2{}^{+\bullet}$ ions in the high-resolution CI spectrum of $O_3/O_2/H_2O$. (b) TQ mass spectrum of the charged products from the reaction of mass-selected $O_3{}^{+\bullet}$ ions (*m/z* 48) with H_2O. In addition to the products of interest, note peaks at *m/z* 36 and 37 ($H_3O–OH^{+\bullet}$ and $(H_2O)_2H^+$) from consecutive reactions of $H_2O–O_2{}^{+\bullet}$ with H_2O.

The occurrence of reaction (1) was confirmed by TQMS. The $O_3{}^{+\bullet}$ ion, generated in the external CI source and mass-selected by the first quadrupole, was allowed to react with neutral H_2O admitted into the collision cell. Both the products traceable to the typical O_2- and O-transfer ability of the $O_3{}^{+\bullet}$ cation were observed (Fig. 1b): $H_2O–O_2{}^{+\bullet}$ at *m/z* 50 and $H_2O_2{}^{+\bullet}$ at *m/z* 34. The latter points to reaction (1) as a route to $H_2O_2{}^{+\bullet}$ ions in $O_3/O_2/H_2O$ ionized mixtures, where $H_2OO^{+\bullet}$ is the most likely initial product.

The $H_2O_2{}^{+\bullet}$ ions, generated in the source of the multisector mass spectrometer, were then mass- and energy-selected, and their CAD spectrum was recorded in the TOF sector of the instrument. It shows peaks at *m/z* 16 ($O^{+\bullet}$), 17 (OH^+), 18 ($H_2O^{+\bullet}$), 32 ($O_2{}^{+\bullet}$) and 33 ($HO_2{}^+$) (Fig. 2). The most abundant fragment, $H_2O^{+\bullet}$, is consistent with $H_2O_2{}^{+\bullet}$ ions of $H_2O–O$ connectivity. Informative fragments also are $O_2{}^{+\bullet}$ and $HO_2{}^+$, that hint at a bound structure, and the OH^+ fragment, traceable to the isomeric $HOOH^{+\bullet}$ ion.

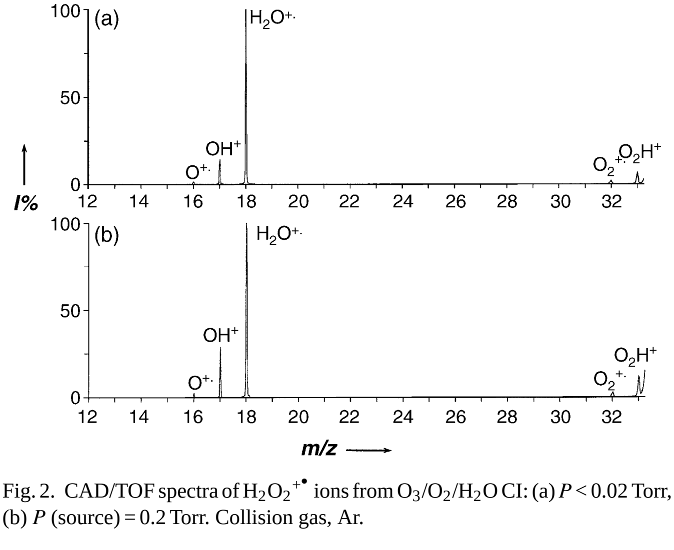

Fig. 2. CAD/TOF spectra of $H_2O_2{}^{+\bullet}$ ions from $O_3/O_2/H_2O$ CI: (a) $P < 0.02$ Torr, (b) P (source) = 0.2 Torr. Collision gas, Ar.

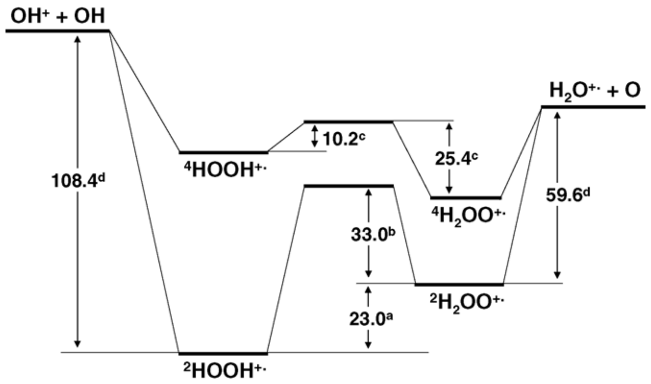

Fig. 3. Energy profile (ΔH°, kcal mol^{-1}) relevant to the doublet and quartet $H_2O_2^{+\bullet}$ ions. (a) From Ref. [3], values ranging from 20 to 24 kcal mol^{-1} are reported in Refs. [1,4,6]. (b) From Ref. [3], values ranging from 33 to 37 kcal mol^{-1} are reported in Refs. [4–6]. (c) From Ref. [6]. (d) From experimental available data [10,11].

These spectral features are in keeping with formation of the oxywater cation and its isomerization to $HOOH^{+\bullet}$ on the $H_2O_2^{+\bullet}$ potential energy surface. Fig. 3 shows the energy profile of the doublet and quartet surfaces. By an estimate of H_f° of $^2H_2OO^{+\bullet}$ based on the computed $^2H_2OO^{+\bullet}$–$^2HOOH^{+\bullet}$ energy difference, 23 kcal mol^{-1}, the exothermicity of reaction (1) can be approximately estimated at 30 kcal mol^{-1} [10,11]. The computed value for the isomerization barrier ranges from 33 to 37 kcal mol^{-1} [3–6]. Although the combination of experimental and theoretical data has at best to be used with caution, it is reasonable to assume that a fraction of the initially formed $^2H_2OO^{+\bullet}$ ions isomerizes to $^2HOOH^{+\bullet}$. As to the quartet surface, Yanez and co-workers reported a computed energy difference of 28.9 kcal mol^{-1} between $^4H_2OO^{+\bullet}$ and $^2H_2OO^{+\bullet}$, and a barrier of 25.4 kcal mol^{-1} to the isomerization of $^4H_2OO^{+\bullet}$ to the less stable $^4HOOH^{+\bullet}$ [6]. On this basis, $^4H_2OO^{+\bullet}$ would be bound by some 30 kcal mol^{-1} with respect to the lowest dissociation into $H_2O^{+\bullet}$ + O(^{3}P), and reaction (1) can be evaluated to be slightly exothermic [10,11]. Thus, vibrationally excited $O_3^{+\bullet}$ ions could generate $^4H_2OO^{+\bullet}$ ions possibly below the isomerization barrier [12].

In this light, the $H_2O^{+\bullet}/OH^+$ ratio recorded in the CAD of $H_2O_2^{+\bullet}$ can be taken as indicative of the presence of the $H_2OO^{+\bullet}$ and $HOOH^{+\bullet}$ ions, though with some approximations. It must be noted indeed that the dissociation into $H_2O^{+\bullet}$ could be favored because it is the lowest energy path, moreover OH^+ could be also formed by consecutive dissociations of $H_2O^{+\bullet}$. The extent of fragmentation of $H_2O^{+\bullet}$ can be inferred from CAD spectra of ion–molecule complexes $[H_2O–M]^+$ (M = O_2, NO_2, NO), whose H_2O moiety retains its identity. Under the same experimental conditions, the $H_2O^{+\bullet}/OH^+$ ratio was about 20/1. Compared to the ratios recorded in the CAD of $H_2O_2^{+\bullet}$ and reported in Table 1, this ratio indicates that the dissociation of $H_2O^{+\bullet}$ does not play a significant role.

On inspection of Table 1, it may be seen that the $H_2O^{+\bullet}/OH^+$ ratio is quite constant in the pressure range 0.1–0.3 Torr, whereas it increases at lower pressures. Moreover the lowest and highest attainable values are very reproducible, and do not significantly change on varying the collision gas (He and Ar). The higher ratio observed at low pressure can be traced to the higher sensitivity of the lowest energy dissociation to the internal energy of the precursor ions, conversely, it could be due to a different composition of the $H_2O_2^{+\bullet}$ mixture formed in the source. As an example, the access to the quartet surface can give $^4H_2OO^{+\bullet}$ ions not viable to the isomerization and hence lead to an ionic population poorer in $HOOH^{+\bullet}$ ions.

Experiments illustrated in the next sections will better elucidate the energetic and structural factors involved in the CAD assay of $H_2O_2^{+\bullet}$, eventually pointing to the oxywater cation as a significant component of the $H_2O_2^{+\bullet}$ mixture formed by $O_3/O_2/H_2O$ CI.

3.2. $H_2O_2^{+\bullet}$ ions in ionized O_2/H_2O mixtures

$H_2O_2^{+\bullet}$ ions were previously observed by CI of O_2/H_2O, although their structure and formation route were not identified [13]. In our high-resolution CI mass spectra, the ratio between the $^{16}O^{18}O^{+\bullet}$ and $H_2O_2^{+\bullet}$ ions was generally higher than in O_3/O_2 CI, ranging from 1 to 5 as the pressure increases. Additional experiments were performed utilizing $^{18}O_2/H_2{}^{18}O$ mixtures. The $H_2{}^{18}O_2^{+\bullet}$ product was unaffected by isobaric contaminations, giving a single peak at *m*/*z* 38. Only under high pressure conditions, it was separated by a low percentage of $H_3{}^{18}O–OH^{+\bullet}$.

Fig. 4a–c show the CAD spectra of $H_2O_2^{+\bullet}$ and $H_2{}^{18}O_2^{+\bullet}$. Compared to those obtained by O_3/O_2 CI, they are much the same, the $H_2O^{+\bullet}/OH^+$ ratio displays the same trend as a function of pressure, and the same slight differences on varying the collision gas (Table 1). The picture appears therefore identical to the chemical ionization of O_3/O_2. $O_3^{+\bullet}$ ions are actually formed by ionization of O_2 plasmas, their intensity being lower than in CI of O_3/O_2, which can account for the minor efficiency of the $H_2O_2^{+\bullet}$ formation. In our conditions, the $O_2^{+\bullet}/O_3^{+\bullet}$ ratio in O_2 CI was only 10–20 times (depending on the pressure) higher than in O_3/O_2 CI.

On the other hand, the formation of $H_2O_2^{+\bullet}$ is highly endothermic from both $O_2^{+\bullet}$ and $H_2O^{+\bullet}$, and a different reac-

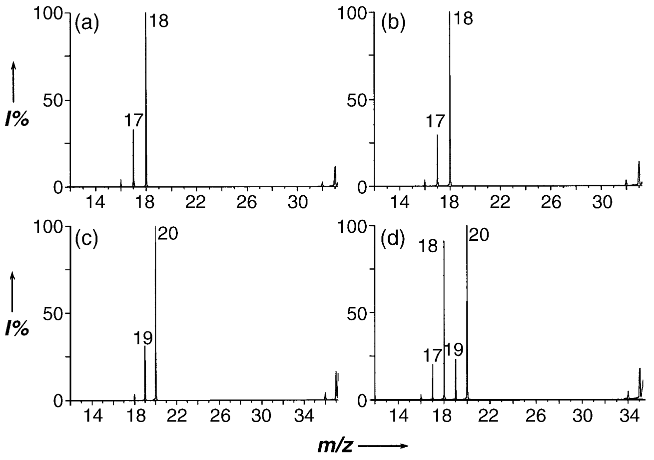

Fig. 4. CAD/TOF spectra of $H_2O_2^{+\bullet}$ ions from (a) O_2/H_2O CI (*m*/*z* 34: collision gas, He), (b) O_2/H_2O CI (*m*/*z* 34: collision gas, Ar), (c) $^{18}O_2/H_2{}^{18}O$ CI (*m*/*z* 38), (d) $O_2/H_2{}^{18}O$ CI (*m*/*z* 36). *P* (source) = 0.2 Torr.

Table 1
$H_2O^{+\bullet}/OH^+$ ratios in CAD spectra of $H_2O_2^{+\bullet}$ ions from ionization of different gaseous mixtures[a]

	Mixture									
	$O_3/O_2/H_2O$		O_2/H_2O		$^{18}O_2/H_2{}^{18}O$		$CH_3OH/^{18}O_2$		$CH_2O/^{18}O_2$	
Collision gas	He	Ar	He	Ar	He	Ar	He	Ar	He	Ar
$P = 0.1–0.3$ Torr	3.1	3.5	3.1	3.8	3.0	3.4	1.0	2.1	1.1	2.4
$P \approx 0.02$ Torr	6.2	7.0	6.4	7.2	7.0	6.8	2.3	3.3	2.5	4.3

[a] Maximum uncertainty, ±10%.

tion route could be only envisaged from electronically excited $O_2^{+\bullet}$ ions. It is known indeed that a large fraction of $O_2^{+\bullet}$ ions formed by electron ionization of O_2 populate the long-lived a $^4\Pi_u$ state [14]. At the low pressure typical of electron impact (≈1 mTorr), $O_2^{+\bullet}$ ($^4\Pi_u$, ν') ions generate $O_3^{+\bullet}$ through an O_4^+ intermediate experimentally identified by mass spectrometry [15–17]. Under these conditions we were able to measure the highest $H_2O^{+\bullet}/OH^+$ ratio, ca. 9, in the CAD of the $H_2O_2^{+\bullet}$ ions. The direct formation of $^2H_2OO^+$ from $O_2^{+\bullet}$ ($^4\Pi_u$, ν') can be evaluated ≥ 22 kcal mol^{-1} exothermic [11,12,18], although no evidence of a possible interaction of $O_2^{+\bullet}$ ($^4\Pi_u$) with water could be obtained. Also, to the best of our knowledge no data is available on the reactivity of $O_2^{+\bullet}$ ($^4\Pi_u$) with water, including charge transfer processes. Nonetheless, reactive interactions with neutrals were found to be one of the mechanisms of quenching of $O_2^{+\bullet}$ ($^4\Pi_u$), effective with species that cannot give resonant charge transfer (i.e., CO, H_2), and hence undergo reactions that are endothermic with $O_2^{+\bullet}$ (X $^2\Pi_g$) [19].

Although additional formation routes could not be identified, a deeper insight was gained by the analysis of $H_2{}^{18}OO^{+\bullet}$ ions (*m*/*z* 36) in $O_2/H_2{}^{18}O$ mixtures. From the abundance of $H_2O_2^{+\bullet}$ (formed from reactions with residual H_2O) it can be evaluated that the contribution of its natural isotopomer (*m*/*z* 36) is less than 0.1% of the peak of interest. Moreover, the formation of "exchanged" $H_2O^{18}O^{+\bullet}$, by direct reaction of labelled $O_n^{+\bullet}$ ($n = 2, 3$) ions with residual H_2O, can be excluded based on the following two lines of evidence. First, no $O_3^{+\bullet}$ labelled ions were observed, and secondly no $H_2{}^{18}O_2^{+\bullet}$ ions (*m*/*z* 38) were observed, coming from possible reactions of $O^{18}O^{+\bullet}$ with the more abundant $H_2{}^{18}O$. Thus, any $H_2O^{18}O^{+\bullet}$ ion can only originate from intramolecular reorganization of the initially formed $H_2{}^{18}OO^{+\bullet}$ ions.

Fig. 4d shows the CAD spectrum of the $H_2{}^{18}OO^{+\bullet}$ ions at *m*/*z* 36. The total $H_2O^{+\bullet}/OH^+$ ratio and its variation are very much in line with the other results, ranging from ca. 4 to 7 as the source pressure is lowered. The isomerized $H^{18}OOH^{+\bullet}$ ions dissociate into $^{18}OH^+$ (*m*/*z* 19) and OH^+ (*m*/*z* 17) fragments, and comparable intensities of the $H_2{}^{18}O^{+\bullet}$ and $H_2O^{+\bullet}$ fragments are also observed.[1] The extensive skeletal randomization, occurring within the source and possibly during the flight, confirms that the $H_2OO^{+\bullet}$ ions are formed just close to the isomerization barrier. Moreover the result shows that "non isomerizing" ions, such as $^4H_2OO^{+\bullet}$, must be a negligible fraction.

In summary, ionization of $O_3/O_2/H_2O$ and O_2/H_2O mixtures allows direct access to the oxywater cation in the $H_2O_2^{+\bullet}$ potential energy surface. The observation of $HOOH^{+\bullet}$, formed by isomerization of $H_2OO^{+\bullet}$, provides compelling evidence for the formation of the oxywater cation. Notwithstanding, very different spectral features characterize $H_2O_2^{+\bullet}$ mixtures enriched by $HOOH^{+\bullet}$, as demonstrated by experiments illustrated in the following.

3.3. $H_2O_2^{+\bullet}$ ions in ionized CH_3OH/O_2 and CH_2O/O_2 mixtures

$H_2O_2^{+\bullet}$ ions were generated by ionization of CH_3OH/O_2 and CH_2O/O_2 mixtures in the source of the multisector mass spectrometer, most likely by reaction (2):

$$[CH_2O]^{+\bullet} + O_2 \rightarrow H_2O_2^{+\bullet} + CO \qquad (2)$$

Isomeric $HCOH^{+\bullet}$ and $CH_2O^{+\bullet}$ ions are well known to be formed by ionization of methanol and formaldehyde, respectively [20]. $CH_2O^{+\bullet}$ ions were reported to generate $H_2O_2^{+\bullet}$ by reaction with O_2 ($k = 1.1 \times 10^{-10}$ cm^3 s^{-1}), although no structure was assigned to the reaction product [21]. The rather low reaction efficiency (ca. 15%), was attributed to the rearrangement required to generate $H_2O_2^{+\bullet}$ by CO loss. No similar reaction was reported for $HCOH^{+\bullet}$.

In our experiments $H_2O_2^{+\bullet}$ ions were observed when utilizing both CH_2O and CH_3OH, although it cannot be excluded that reaction (2) is undergone by only one reactant ion, albeit present in different proportions in the two mixtures. The observation of $H_2{}^{18}O_2^{+\bullet}$ at *m*/*z* 38 in $CH_3OH/^{18}O_2$ and $CH_2O/^{18}O_2$ mixtures confirmed the loss of carbon monoxide from the ionic reactant. Moreover, using $^{18}O_2$ prevented possible incursion of reaction (1) from water.

Confirming experiments were performed by TQMS. Ions at *m*/*z* 30 were generated by ionization of CH_3OH and CH_2O in the external source, then isolated and reacted with O_2. $H^{13}CO^+$ ions were likely present in the selected ionic population, however the formation of $H_2O_2^{+\bullet}$ ions (together with HCO^+ at *m*/*z* 29) can be only traced to the $CH_2O^{+\bullet}$ and/or $CHOH^{+\bullet}$ reactant ions (Fig. 5).

The CAD/TOF spectra of $H_2O_2^{+\bullet}$ from both CH_3OH/O_2 and CH_2O/O_2 mixtures are reported in Fig. 6. They are closely similar, but very different from those of $H_2O_2^{+\bullet}$ ions produced by reaction (1). The $H_2O^{+\bullet}/OH^+$ ratio is close to the unity when Helium is used as a collision gas and decidedly increases with Argon (Table 1). It remains regardless lower than those recorded in H_2O/O_2 CI under the same experimental conditions (source pressure, collision gas). These spectral features are suggestive

---

[1] Slight variations with pressure cannot be distinguished from possible isotope effects.

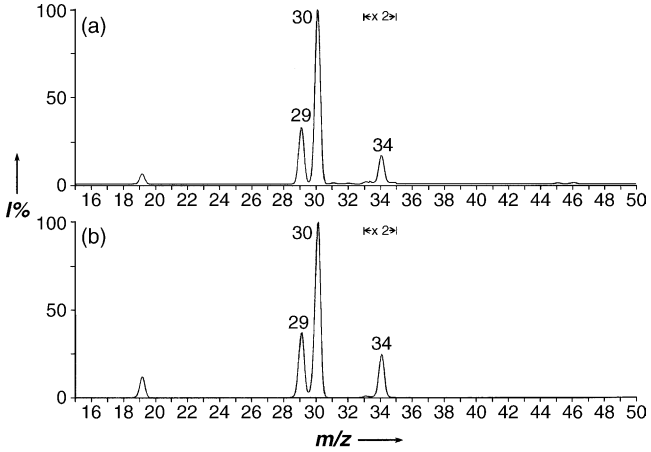

Fig. 5. TQ mass spectrum of the charged products from the reaction of mass-selected $CH_2O^{+\bullet}$ ions (*m/z* 30) with O_2: (a) $CH_2O^{+\bullet}$ ions from CH_3OH/EI; (b) $CH_2O^{+\bullet}$ ions from CH_2O/EI.

of $HOOH^{+\bullet}$ ions that largely decompose through their own structure and point to a different composition of the $H_2O_2^{+\bullet}$ population with respect to the $O_3/O_2/H_2O$ CI. Remarkably, the dissociation into OH^+ appears even more extensive than from $H_2O_2^{+\bullet}$ ions directly obtained by ionization of hydrogen peroxide.

Although the mechanism of formation of $H_2O_2^{+\bullet}$ in these plasmas is not known, arguably a concerted reaction from either *cis*-$HCOH^{+\bullet}$ or $CH_2O^{+\bullet}$ can be conducive to $HOOH^{+\bullet}$ ions. As anticipated, the $H_2O^{+\bullet}$ fragment cannot be exclusively attributed to $H_2OO^{+\bullet}$, because it corresponds to the lowest dissociation limit. On the basis of available experimental and theoretical data [1,10,22], ΔH° of reaction (2) can be evaluated ca. -49 and $-42\,\text{kcal mol}^{-1}$ from the two reactant ions, respectively. Nonetheless, the reaction could require to overcome a barrier, and the energy content of the $HOOH^{+\bullet}$ ions could be sufficient to undergo the isomerization to $H_2OO^{+\bullet}$, whose presence in the ionic population cannot be accordingly excluded.

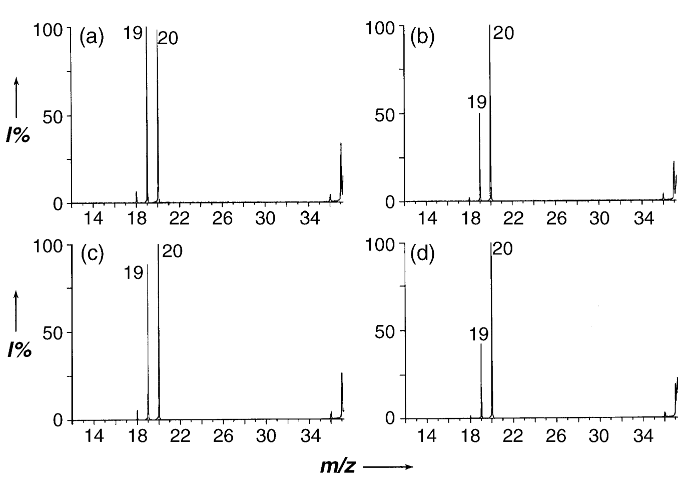

Fig. 6. CAD/TOF spectra of $H_2O_2^{+\bullet}$ ions from $CH_3OH/^{18}O_2$ CI: (a) collision gas, He; (b) collision gas, Ar; and from $CH_2O/^{18}O_2$ CI; (c) collision gas, He; (d) collision gas, Ar. *P* (source) = 0.2 Torr.

However, at variance with $H_2OO^{+\bullet}$ that directly dissociates to $H_2O^{+\bullet}$, $HOOH^{+\bullet}$ can do it only by isomerization after collision. The latter process is likely to be sensitive to the collision gas, since larger energy transfers favour direct fragmentation with respect to isomerization [23]. Consistent with this view, the $H_2O_2^{+\bullet}$ ions produced by reactions (2) and (1) display considerably different sensitivity to the collision gas (Table 1). When $H_2O_2^{+\bullet}$ is formed by reaction (2), the $H_2O^{+\bullet}$ fragment largely derives from isomerization of $HOOH^{+\bullet}$ and hence it is favored by Argon, whereas the direct fragmentation to OH^+ is favored by Helium. By contrast, when $H_2O_2^{+\bullet}$ is formed by reaction (1), the dissociation into $H_2O^{+\bullet}$ largely derives from direct fragmentation, and collision effects are less significant with respect to the processes occurring in the source. On the whole, in addition to the structural analysis, such a difference marks the entrance channel of the reported reactions, that form $H_2O_2^{+\bullet}$ mixtures particularly enriched by $HOOH^{+\bullet}$ (reaction (2)) and $H_2OO^{+\bullet}$ (reaction (1)) ions, respectively.

Energetic factors are instead likely to account for the increase of the $H_2O^{+\bullet}/OH^+$ ratio, that is always observed at lower pressures, irrespective of the formation route of $H_2O_2^{+\bullet}$. This finding conceivably suggests that the lowest energy dissociation path is favored at higher internal energies of the precursor ions.

4. Conclusions

The oxywater cation $H_2OO^{+\bullet}$ was directly generated in the gas phase, by the reaction of $O_3^{+\bullet}$ with water. Different mixtures of $H_2O_2^{+\bullet}$ ions, rich in either the $HOOH^{+\bullet}$ or the $H_2OO^{+\bullet}$ isomer, were obtained and characterized by mass spectrometric techniques. Structural and energetic effects have been found to play a role in the analysis of $H_2O_2^{+\bullet}$ ions by CAD mass spectrometry.

Acknowledgments

Financial support by the Italian Government (COFIN-FIRB) and Rome University "La Sapienza". We thank Stefania Recaldin for editorial assistance.

References

[1] M.J. Frisch, K. Raghavachari, J.A. Pople, W.J. Bouma, L. Radom, Chem. Phys. 75 (1983) 323.
[2] B.F. Yates, W.J. Bouma, L. Radom, Tetrahedron 42 (1986) 6225.
[3] Y. Xie, W.D. Allen, Y. Yamaguchi, H.F. Schaefer III, J. Chem. Phys. 104 (1996) 7615.
[4] D. Schröder, C.A. Schalley, N. Goldberg, J. Hrůsák, H. Schwarz, Chem. Eur. J. 2 (1996) 1235.
[5] B.S. Jursic, J. Mol. Struct. (THEOCHEM) 401 (1997) 45.
[6] A.I. Gonzalez, O. Mo, M. Yanez, Anales de Quimica Int. Ed. 93 (1997) 310.
[7] K.M. Stirk, L.K. Marjatta Kiminkinen, H.I. Kenttämaa, Chem. Rev. 92 (1992) 1649.
[8] P.T. Buckley, J.W. Birks, Atmos. Environ. 29 (1995) 2409.
[9] G. de Petris, Mass Spectrom. Rev. 22 (2003) 251 (and references therein).

[10] NIST Chemistry WebBook. NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 2003.

[11] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (suppl. 1) (1988).

[12] J.T. Moseley, J.-B. Ozenne, P.C. Cosby, J. Chem. Phys. 74 (1981) 337 (the lowest dissociation energy of $O_3^{+\bullet}$ $X(^2A_1)$ is 0.6 eV).

[13] R. Susič, B. Kralj, D. Žigon, Rapid Commun. Mass Spectrom. 9 (1995) 64.

[14] B.R. Turner, J.A. Rutherford, D.M.J. Compton, J. Chem. Phys. 48 (1968) 1602.

[15] J.M. Ajello, K.D. Pang, K.M. Monahan, J. Chem. Phys. 61 (1974) 3152.

[16] P.M. Dehmer, W.A. Chupka, J. Chem. Phys. 62 (1975) 2228.

[17] F. Cacace, G. de Petris, M. Rosi, A. Troiani, Chem. Eur. J. 8 (2002) 3653.

[18] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, 1978.

[19] W. Lindinger, D.L. Albritton, M. McFarland, F.C. Fehsenfeld, A.L. Schmeltekopf, E.E. Ferguson, J. Chem. Phys. 62 (1975) 4101.

[20] P.C. Burgers, A.A. Mommers, J.L. Holmes, J. Am. Chem. Soc. 105 (1983) 5976.

[21] N.G. Adams, D. Smith, D. Grief, Int. J. Mass Spectrom. Ion Proc. 26 (1978) 4059.

[22] W.J. Bouma, P.C. Burgers, J.L. Holmes, L. Radom, J. Am. Chem. Soc. 108 (1986) 1767.

[23] R.G. Cooks, Collision Spectroscopy, Plenum Press, New York, 1978.