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A mass spectrometric and computational study of gaseous peroxynitric acid and $(HOONO_2)H^+$ protomers

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Abstract

The positive ion chemistry of peroxynitric acid (**1**) was investigated in the gas phase by mass-analyzed ion kinetic, collisionally activated dissociation, and Fourier transform-ion cyclotron resonance mass spectrometric techniques and theoretical methods up to the B3LYP/6-311++g(3*df*,2*pd*) and G2, i.e. QCISD(T)/6-311+g(3*df*,2*pd*), levels. The ion–neutral complex HOOH–NO_2^+ (**1a**) is the only detectable protomer in CI experiments involving the protonation of **1** by H_3O^+, and can also be obtained from the reaction of NO_2^+ with H_2O_2. **1a** behaves as a protonating and nitrating agent toward gaseous nucleophiles. The experimental proton affinity of **1** is estimated to be 176 ± 3 kcal mol^{-1}, in excellent agreement with the 175 ± 2 kcal mol^{-1} G2 PA. The theoretical results show that **1a** is more stable than the $HOONO_2H^+$ (**1b**) and the $H_2OONO_2^+$ (**1c**) protomers by 13 and 16 kcal mol^{-1}, respectively, at the B3LYP level of theory, and account for the exclusive formation of **1a** in the CI experiments. The experimental and B3LYP theoretical binding energy of NO_2^+ to H_2O_2 amounts to 18 ± 2 kcal mol^{-1}. (Int J Mass Spectrom 195/196 (2000) 1–10) © 2000 Elsevier Science B.V.

Keywords: Peroxides; Gas-phase chemistry; Mass spectrometry; Ab initio and DFT calculations; Ion–neutral complexes

1. Introduction

Peroxynitric acid ($HOONO_2$, **1**) is an important component of the earth's atmosphere generated by a reactive combination of HO_2 and NO_2 radicals [1–4]. In the past 20 years such species has been extensively investigated owing to its intrinsic interest [5] and to its role in atmospheric chemistry and physics [6,7]. Nevertheless, owing to its rather short lifetime [8] and to the difficulties related to its synthesis [9], the available thermodynamic and kinetic data are still relatively scarce.

To the best of our knowledge no computational nor experimental studies on the gas-phase ion chemistry of **1** have been reported. This state of affairs has stimulated the present study, specifically aimed at investigating the protonation of **1**, and evaluating its proton affinity (PA), a fundamental thermochemical quantity that plays a key role in gas-phase acid–base equilibria. Our interest for such species is in line with our previous work in the field of gas-phase ion chemistry recently focused on molecules containing oxygen–oxygen bond [10], in particular, on proto-

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Dedicated to the memory of Professor Robert R. Squires.

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nated NO_2–X systems [11]. In the latter studies the joint application of structurally diagnostic mass spectrometric and computational techniques allowed us to demonstrate the existence and the relative stability of two types of protomers, namely the ion–molecule complex **a** formed by the nitronium ion and the neutral molecule HX, and the NO_2 protonated ion **b**

$$\underset{\textbf{a}}{(HX\text{–}NO_2)^+} \qquad \underset{\textbf{b}}{(XNO_2H)^+}$$

The protomer **a** is the more stable for X = HO, CH_3O [11a,b], whereas for X = NH_2 [11c] the protomer **b** was found to be the preferred one, the stability gap becoming very small when X = C_2H_5O [11d]. The ability of the X moiety to stabilize the positive charge on the covalently bound NO_2H^+ group was identified as the major factor for the stability of the **b** species. On the other hand, for the ion–neutral complex **a** the proton affinity correlates with the X–H and the X–NO_2 bond [11,12].

In this framework, peroxynitric acid, formally a X–NO_2 species with X = HOO, is an interesting system to test the validity of the above mentioned findings, although the situation is somewhat more complicated due to the possible existence of an additional protomer. In fact, three species of different connectivity are conceivable, namely the hydrogen peroxide/NO_2^+ ion–molecule complex **1a**, the nitroprotonated species **1b** and the OH protonated structure **1c**

$$\underset{\textbf{1a}}{(HOOH\text{–}NO_2)^+} \qquad \underset{\textbf{1b}}{(HOONO_2H)^+} \qquad \underset{\textbf{1c}}{(H_2OONO_2)^+}$$

The present study addresses the relative stability of the above mentioned protomers and their intramolecular interconversion. The matters are examined in the framework of the previous results on the protonated X–NO_2 analogues.

2. Experimental and methods of calculation

2.1. Materials

Peroxynitric acid was obtained from the reaction of $NaNO_2$ with hydrogen peroxide in aqueous $HClO_4$ solution, as described in [9b]. The vapor over the crude reaction mixture was employed for the mass spectrometric experiments.

2.2. Mass spectrometric measurements

The experiments were performed on a ZAB-2F and a model Quattro Triple Quadrupole (TQ) spectrometers from VG Micromass Ltd and on a 47e model Fourier transform-ion cyclotron resonance (FTICR) instrument from Bruker Spectrospin AG equipped with an “infinity” cell and an external EI/CI ion source.

Because of the rapid decomposition of **1** and its low vapor pressure from the aqueous solution, its actual insertion into the magnetic instrument required a specially built direct insertion probe, which could be cooled to, and thermostated at, any temperature down to −80 °C. In this way the peroxynitric acid vaporized directly from the solution introduced in a capillary glass tube into the ion source without any contact with the metal walls of conventional reservoirs and vacuum lines. In the TQ experiments the vapor over the reaction mixture was driven into the source via a home-built liquid insertion probe equipped with an external glass tube connected by a valve to the ion source through a very short metal line. The above mentioned insertion probes were also used for model experiments involving the nitration of hydrogen peroxide from a 40% aqueous solution of H_2O_2 containing a small concentration of nitric acid.

Protonation of peroxynitric acid was obtained in the CI/CH_4 of **1** by the proton transfer occurring almost exclusively from the H_3O^+ ions generated from the protonation of the large excess of H_2O contained in the synthetic mixture used as the source of the acid.

2.2.1. MIKE and CAD experiments

Typical experimental conditions were as follows: CH_4 pressure, 0.2 Torr; source temperature, 160 °C; repeller voltage, 0 V; emission current, 0.5–1 mA; accelerating voltage, 8 kV. Helium, used as the target gas to record the collisionally activated dissociation (CAD) spectra was admitted into the collision cell to a pressure ensuring a 30% reduction of the main beam intensity, each spectrum being the average of 50 scans. Analogous experiments were performed to obtain the CAD spectra of the model ion **1a** produced by nitration of H_2O_2 from a H_2O_2/HNO_3 solution.

2.2.2. TQ experiments

The low-energy CAD spectra of $(HOONO_2)H^+$ were recorded by generating the protonated **1** under the following experimental conditions: CH_4 pressure, ~0.1 Torr; source temperature, 150 °C; repeller voltage, 0 V. After mass selection by the first quadrupole (Q1), the $HOONO_2H^+$ ions were driven into the collision cell Q2 (a hexapolar rf-only cell) and hence accelerated to different axial kinetic energies [13] and allowed to collide with the target gas (Ar) at a thickness not exceeding 9×10^{-12} cm^2 in order to minimize multiple-collision phenomena. The ionic products were finally analyzed by the third quadrupole (Q3) used in the scan mode at a standard frequency of 150 u s^{-1}. Each experiment included 50 scans and was repeated twice in order to check its reproducibility.

Analogous experiments were performed to obtain the CAD spectra of the model ion **1a** produced by nitration of H_2O_2 from a H_2O_2/HNO_3 liquid mixture, as well as to deduce the H_2O_2–NO_2^+ binding energy (BE) by the kinetic method [14] using different nucleophiles [CH_3OH, C_2H_5OH, CH_3CN, $(CH_3)_2CO$, $(C_2H_5)_2O$] as ligands L, as illustrated in the next subsection.

To ascertain whether the observed $(HOONO_2)H^+$ were actually formed from **1**, the presence of the latter in the source was controlled by negative N_2O/CH_4/CI of the aqueous solution of the acid, carried out under conditions analogous to those used in the positive chemical ionization. In addition to the ions formed from nitric acid, a sharp signal at *m/z* 79 with a 100 eV CAD characterized by the presence of the NO_2^- fragment at *m/z* 46 was observed, which positively established the presence of the $HOONO_2^-$ radical anion and hence of its neutral parent **1**. On the other hand, no signal at *m/z* 79 was formed in the negative N_2O/CH_4/CI of the H_2O_2/HNO_3 mixture used for generating the model ion **1a**.

2.2.3. TQ kinetic method

The L–NO_2^+ ions, generated in the CI source by ligand-exchange reaction between protonated nitric acid and the neutral species L, were mass selected and accelerated into the collision cell containing Ar at pressure up to 2×10^{-5} Torr in order to avoid multiple-collision processes. The accelerating voltage was chosen in such a way to obtain a nominal 3.0 eV center-of-mass collision energy for all the L–NO_2^+ Ar pairs. The I intensities of the L–NO_2^+ ions were normalized to their I_0 initial intensities (no Ar admitted in the cell) and plotted versus the target thickness S, which represents the number of the target gas molecules per square centimeter of the cell. According to the equation $\ln I/I_0 = e^{-S\sigma}$, the σ cross sections for the dissociation process $L\text{–}NO_2^+ + Ar \rightarrow L + NO_2^+ + Ar^*$ were obtained and utilized to construct a calibration plot of σ versus the known BE. By a best fitting procedure, the binding energy of NO_2^+ to hydrogen peroxyde has been deduced from the measured cross section of the dissociation process of **1a** ions generated in the protonation of peroxynitric acid.

2.2.4. FTICR experiments

The reactions of the $(HOONO_2)H^+$ ions were investigated utilizing the CI source of the FTICR spectrometer operating at a total pressure not exceeding 7×10^{-5} Torr. After isolation by "soft" ejection techniques, the ions at *m/z* 80, thermalyzed by collisions with Ar introduced via a pulsed valve, were driven into the resonance cell and allowed to react with the nucleophile/base, namely $C_2H_5NO_2$, CH_3NO_2, CCl_3CN, and H_2O at a pressure of $\sim 10^{-8}$ Torr.

2.3. Computational details

Two different aspects were addressed. First, the critical points corresponding to the structures **1**, **1a**, **1b**, **1c**, and the interconnecting **TS**s were optimized by using electronic energies, analytical gradients and Hessian matrixes calculated in the framework of the density functional theory utilizing the B3LYP hybrid functional [15] with the standard 6-311++g($3df$,$2p$) basis set [16]. Second, the proton affinity of **1** was obtained performing calculations on each of the absolute minima found on the $HOONO_2$ and the $(HOONO_2)H^+$ hypersurfaces using two approaches: 1–coupled cluster singles doubles (triples) [CCSD(T)] calculations [17], i.e., restricted coupled cluster singles and doubles approach calculating the connected triples by perturbation theory with the cc-pVTZ [18] basis set at the B3LYP/6-311++g(3*df*,2*pd*) optimized geometries; 2–QCISD(T)/6-311+g(2*df*,*p*) calculations adopting the G2 procedure [19].

The thermal corrections to 298 K were calculated with a standard statistical mechanical formula [20] by using the calculated moments of inertia and harmonic frequencies. The reliability of the above mentioned levels of theory in deriving thermochemical properties, although well documented [21], were specifically tested in the present study by calculating the proton affinity of the nitric acid, selected mainly for its structural and chemical similarity to peroxynitric acid. All calculations were performed using the GAUSSIAN 94 [22] and MOLPRO 96 [23] packages.

3. Results and discussion

3.1. Protonated peroxynitric acid

3.1.1. Mass spectrometric investigation

The investigation of the ionic population of $(HOONO_2)H^+$ was initially performed by triple quadrupole experiments. A signal at *m/z* 80, although not very intense, could be detected in the plasma and structurally analyzed by CAD spectrometry, recording the spectra at absolute translational energies up to 100 eV and with a collision gas pressure of 10^{-5} Torr. These conditions were chosen as a good balance between a sufficiently extensive fragmentation and a noise/signal ratio lower than 10% of the overall ionic beam's signal.

The results of the above mentioned experiments, collected in Table 1, show the formation of the fragment at *m/z* 46 (assigned as NO_2^+) together with the small but sharp fragment at *m/z* 34 corresponding to the $H_2O_2^+$ radical ion obtained from excited electronic states [24] generated at higher collision energies.

Table 1
Low-energy CAD spectra of $H_2NO_4^+$ ions

Formation process	Collision energy (eV)	Relative intensity of fragments (%)[a]	
		m/z = 34	*m/z* = 46
Protonation of $HOONO_2$	50	. . .	100
	80	3	97
	100	9	91
Nitration of H_2O_2	50	. . .	100
	80	2	98
	100	6	94

[a] Standard deviation ~15%.

These results suggest that the $HOOHNO_2^+$ ions from protonation of **1** have the ion–neutral structure **1a**. This inference is supported by the superimposable CAD spectra of the $H_2NO_4^+$ ions from the protonation of **1** and the nitration of hydrogen peroxide, although the latter process is expected to yield the model ion **1a**. It is appropriate here to address a problem related to the (necessarily) crude nature of the CI experiments whereby the vapors over a solution of **1**, prepared from sodium nitrite, hydrogen peroxide, and perchloric acid, were introduced directly into the ion source. It is conceivable that under these conditions the population of $(HNO_4)H^+$ ions from protonation of **1** may be contamined to some extent by $H_2NO_4^+$ ions from other processes, e.g. from the reaction of H_2O_2 vapors with some gaseous nitrating agent. Nevertheless, since the presence of **1** in the vapors introduced into the ion source was positively established by N_2O/CH_4 negative chemical ionization, the conclusion seems warranted that the assignment of the **1a** structure to the $(HNO_4)H^+$ ions from the protonation of **1** represents the most reasonable explanation of the CAD results.

Consistently, the mass-analyzed ion kinetic (MIKE) spectra of the ions at *m/z* 80 formed in the CI/CH_4 of peroxynitric acid display only the fragment at *m/z* 46 corresponding to NO_2^+, which arises from the H_2O_2 loss, and the same feature characterizes the MIKE spectra of the model ion $HOOHNO_2^+$ generated from the nitration of H_2O_2. In both cases, the meta-

Table 2
High-energy CAD spectra of $H_2NO_4^+$ ions

Formation process	Relative intensity of fragments (%)[a]				
	$m/z = 18$	$m/z = 30$	$m/z = 33$	$m/z = 34$	$m/z = 63$
Protonation of $HOONO_2$	4	30	6	56	4
Nitration of H_2O_2	4	25	5	63	3

[a] Standard deviation ~10%.

stable NO_2^+ peak is particularly narrow, suggestive of a substantially low kinetic energy release, typical of a simple bond fission.

Passing to the high energy (8 keV) fragmentation, the CAD spectra of the ions at *m/z* 80 obtained from the protonation of peroxynitric acid and the nitration of H_2O_2 are very similar and display many fragments (Table 2), the major fragment being the $H_2O_2^+$ ion if one neglects NO_2^+, arising also from the unimolecular dissociation.

Finally, the assignment of the ion–dipole structure is consistent with the FTICR results, in that thermalized $(HOONO_2)H^+$ ions were found to react with $C_2H_5NO_2$ (PA = 183 kcal mol^{-1}), CH_3NO_2 (PA = 179.9 kcal mol^{-1}), and CCl_3CN (PA = 173.4 kcal mol^{-1}) via both H^+ and NO_2^+ transfer, occurring at a ratio of ~1:2, whereas only the nitronium ion transfer was observed to H_2O (PA = 165.2 kcal mol^{-1}) [25].

In summary, all the above mentioned results suggest that structure **1a** can be assigned to protonated peroxynitric acid formed in CI experiments, a conclusion in agreement with the theoretical results illustrated in the following.

3.1.2. Computational study

In Table 3 the B3LYP/6-311++g(3*df*,2*pd*) electronic energies and zero point energies [26] are collected for the species **1**, **1a**, **1b**, and **1c** defined for all of their isomers as **1a(i)**, **1b(i)**, and **1c(i)** for **i** ranging from 1 to *N* (*N* = number of conformers) and for the transition structures interconnecting the different minima (**TSb/a** and **TSc/a**) as well. For comparison (see above), the results obtained at the same level of theory for the most stable isomer of protonated nitric acid as well as of the neutral are reported.

The corresponding geometries are depicted in Fig. 1. As already known from the literature [5b], the only minimum corresponding to the neutral peroxynitric acid is the C_1 structure **1**, nearly planar with the exception of the hydrogen atom orthogonal to the plane. The absolute minimum of the overall $[H_2, N, O_4]^+$ surface was found to be the $HOOH–NO_2^+$ ion–neutral complex where only the C_1 bridged-like conformer **1a** was located as a critical point. Structurally, owing to the relatively large distances of more than 2 Å from *N* to both the oxygen atoms of the HOOH moiety, **1a** can be defined as a genuine loosely bound ion–dipole complex. The relatively low value of 18 kcal mol^{-1} for the NO_2^+ and H_2O_2 binding energy at 298 K confirms the previous statement [27].

Moreover, several NO_2-protonated conformers **1b(i)** were located on the same surface. Some of them were found as C_1 structures energetically close to each other being ~13 kcal mol^{-1} less stable than **1a**

Table 3
B3LYP/6-311++g(3*df*,2*pd*) electronic energies (EE), zero point energies (ZPE), enthalpy corrections at 298 K (*E* corr.) and relative enthalpies at 298 K (ΔH)

Species	EE (Hartree)	ZPE (Hartree)	*E* corr. (Hartree)	ΔH (kcal mol^{-1})
$HOONO_2$ (C_1)	−356.157 22	0.029 23	0.035 00	+169
1a (C_1)	−356.438 45	0.040 30	0.047 73	0
1b(1) (C_1)	−356.416 23	0.041 00	0.047 03	+13
1b(2) (C_1)	−356.417 51	0.041 10	0.047 19	+13
1b(3) (C_1)	−356.416 23	0.041 01	0.047 02	+13
1c(1) (C_s)	−356.412 90	0.040 99	0.047 45	+16
1c(2) (C_s)	−356.407 49	0.040 55	0.047 16	+19
TSa/b (C_1)	−356.366 43	0.036 47	0.042 45	+41
TSa/c (C_1)	−356.370 49	0.034 93	0.041 71	+39
H_2O_2 (C_2)	−151.612 83	0.026 58	0.030 74	
NO_2^+ (C_{*v})	−204.795 36	0.011 89	0.015 47	+18[a]
$H_2ONO_2^+$ (C_s)	−281.289 60	0.035 64	0.042 32	0
HNO_3 (C_s)	−281.000 03	0.026 40	0.030 86	+174

[a] This value corresponds to NO_2^+ BE of H_2O_2.

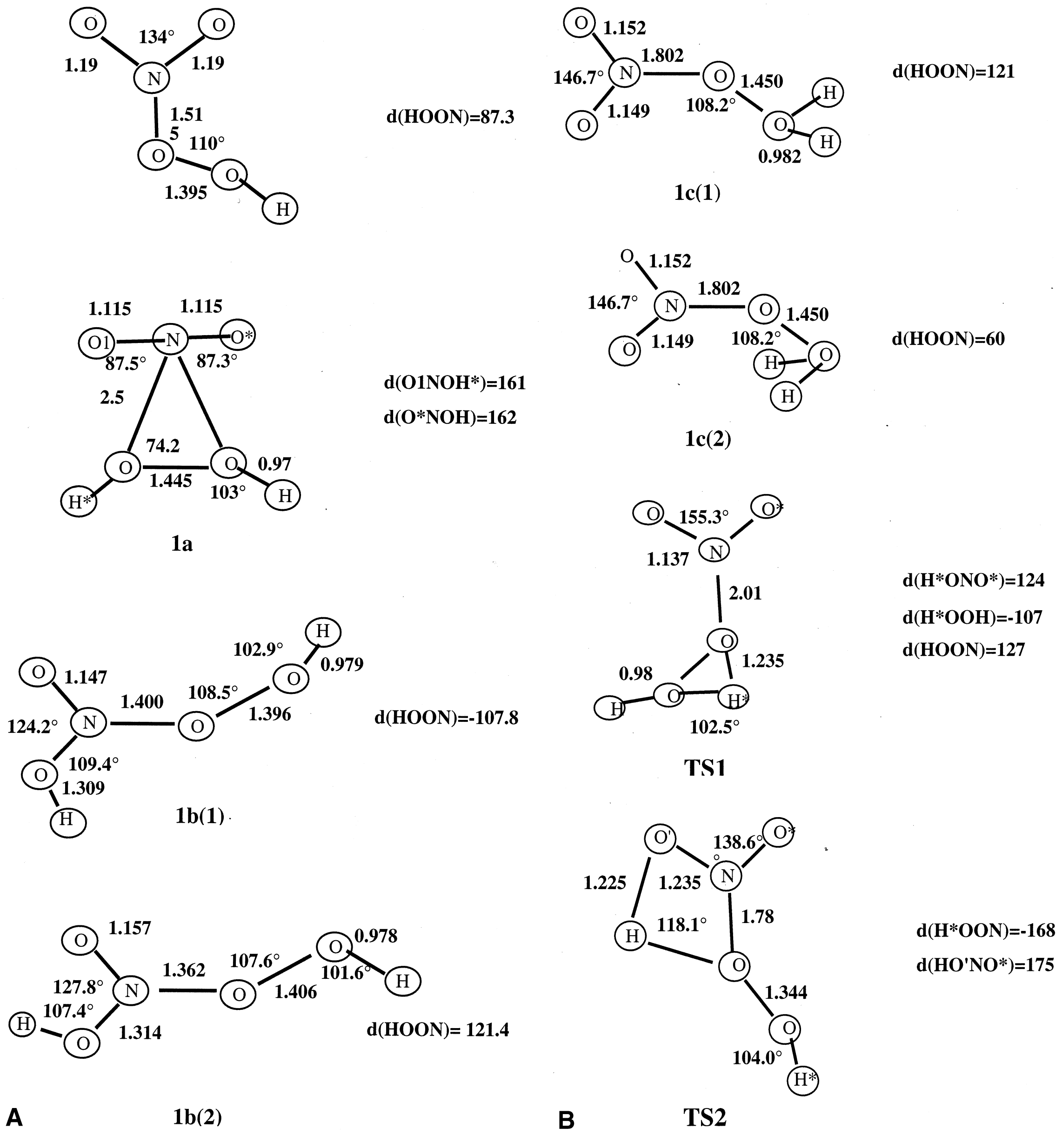

Fig. 1. Geometries of peroxynitric acid and its isoprotomers optimized at the B3LYP/6-311++g(3*df*,2*pd*) level of theory.

at 298 K. Because of the above similarity and expecting no dramatic changes when passing to the other conformers, we considered it unnecessary to extend the study to all the **1b(i)** conformers. In analogy with the NO_2-protonated isomers of $(X–NO_2)H^+$ species, all the **1b(i)** can be described as covalently bound ions on the basis of the length of all of the bonds. Therefore, also in the present case the greater stability of **1a** with respect to all **1b(i)** can be rationalized on the basis of the expectedly scarce ability of the HOO group of stabilizing a positive charge on the $–NO_2H–$ moiety [11,12].

Two **1c(i)** C_s conformers, namely the *anti* and the *gauche* conformers of the HO-protonated isomers energetically slightly less stable than the **1b(i)** conformers were also located on the B3LYP hypersurface.

Finally, the transition structures for the interconversion of **1b(1)** and **1c(1)** into the most stable **1a** isomer, namely the **TSb/a** and **TSc/a** structures are located 29 and 23 kcal mol^{-1} to the **1b(1)** and **1c(1)**, respectively.

The computational results neatly account for the observation that only ions **1a** are detectable in our CH_4/CI experiments where **1** is protonated predominantly by H_3O^+. The lower stability of **1b** and **1c** than of **1a** (Table 3) makes the local PA of the NO_2 group and of the terminal OH group of $HOONO_2$ lower by 13 and 16 kcal mol^{-1}, respectively, than the PA of **1**, referred of course to the most basic site of the molecule, the central O atom, and amounting to ~175 kcal mol^{-1} (vide infra). Thus, protonation by H_3O^+ of the NO_2 group and the terminal OH group, yielding **1b** and **1c**, respectively, is appreciable endothermic, given the PA of H_2O, 165.2 kcal mol^{-1} [25b]. Furthermore, any **1b** and **1c** ions formed, e.g. by direct protonation of **1** by CH_5^+, would be rapidly deprotonated by H_2O, by far the major component of the vapor introduced into the CI source. Since H_3O^+ can exothermically protonate **1**, the reaction of any **1b** and **1c** ions with water can be regarded as an effective way to accomplish their isomerization into the more stable protomer **1a** by an intermolecular process, whereas their intramolecular isomerization seems unlikely, owing to the high barriers (**TS b/a** and **TS c/a** in Table 3).

3.2. PA of peroxynitric acid

3.2.1. Experimental results

Accurate experimental evaluation of the PA of **1** is particularly difficult. The acid cannot be obtained in the pure state and rapidly decomposes, which prevents application of the FTICR equilibrium method [25a,28]

$$BH^+ + HNO_4 \rightleftarrows (HNO_4)H^+ + B \tag{1}$$

Application of the less accurate “bracketing” technique is hampered by the incursion of an unwanted side reaction, i.e. NO_2^+ transfer, to many of the reference bases of appropriate PA. From the many bracketing experiments performed we could only conclude that the PA of **1** exceeds that of H_2O, 165.2 kcal mol^{-1} and is close to that of CCl_3CN, 173.4 kcal mol^{-1} [25b], as suggested by the slow proton transfer from $(HNO_4)H^+$ to the latter base.

Next, the kinetic method based on equilibria of the relative dissociation rate of proton-bound dimers [29,30] was tried and found also unsatisfactory, because $HOOHNO_2^+$ forms both from proton-bound and nitronium-bound dimers.

In view of the above mentioned difficulties, exploiting the ability of the TQ instrument to record low-energy CAD spectra [14,30], we utilized a version of the kinetic method to evaluate the $\Delta H°$ change of the process

$$HOOH\text{–}NO_2^+ \rightarrow H_2O_2 + NO_2^+ \tag{2}$$

namely the 298 K BE of NO_2^+ to H_2O_2, which can allow one to calculate the heat of formation of **1a** ion and consequently the proton affinity of HNO_4.

The evaluation of the NO_2^+/H_2O_2 BE was based on the comparison of the cross section of the collision-induced dissociation

$$(HOOHNO_2^+)^* + Ar \rightarrow H_2O_2 + NO_2^+ + Ar^* \tag{3}$$

undergone by translationally excited **1a** ions with the cross sections of the analogous dissociation processes undergone by LNO_2^+ complexes, where L denotes a ligand of known NO_2^+ BE [31]. Several such complexes were prepared in the CI source of the TQ spectrometer utilizing the ligand-exchange reaction

$$H_2ONO_2^+ + L \rightarrow LNO_2^+ + H_2O \tag{4}$$

chosen as a mildly exothermic route to complexes containing a small and comparable excess of internal energy. From the CAD experiments the absolute cross section for their dissociation processes have been obtained (Table 4) that fitted a reasonably linear correlation (correlation coefficient = 0.961) when

Table 4
Cross sections (σ) for the CAD of L–NO_2^+ complexes and NO_2^+/L binding energy of the L ligands

Species	σ[a] (10^{-14}, cm^2)	NO_2^+ BE[b] (kcal mol^{-1})
H_2O–NO_2^+	8.0 ± 0.7	19.6[c]
CH_3OH–NO_2^+	7.5 ± 0.8	21.5
C_2H_5OH–NO_2^+	4.8 ± 0.8	22.2
CH_3CN–NO_2^+	2.3 ± 0.5	25.5
$(CH_3)_2CO$–NO_2^+	2.2 ± 0.6	25.9
$(C_2H_5)_2O$–NO_2^+	2.0 ± 0.5	27.1

[a] From present study.
[b] From [31].
[c] From [11].

plotted versus the known NO_2^+ BE of the ligands L [31], as shown in Fig. 2. It should be noted in this connection that under our experimental conditions, namely low target gas pressure and minimum collision energy, no differential deposition of the internal energy occurs among the different degrees of freedom, which allowed us to correlate the absolute cross section with the binding energy.

The cross section for process Eq. (3) has been estimated 9.0×10^{-14} cm^2 from the CAD spectra of **1a** ions formed in the protonation of peroxynitric acid, whose structure has been ascertained to correspond to the hydrogen peroxyde/NO_2^+ ion–molecule complex, as described in the previous section. Using this value by standard best fitting procedure we obtained 18 ± 2 kcal mol^{-1} for the NO_2^+/H_2O_2 BE, which in turn has been utilized to calculate the heat of formation of **1a** ion of 179 ± 3 kcal mol^{-1} at 298 K, on the basis of Eq. (2) [25b].

Finally, from the known H_f° of H^+ and **1** [25b,5b], the proton affinity of peroxynitric acid has been evaluated to be 176 ± 3 kcal mol^{-1}. Despite the unusually wide uncertainty range, as large as 6 kcal mol^{-1}, we regard the result as the most reliable experimental estimate in the particularly difficult case of HNO_4. Incidentally, NO_2^+ BE of H_2O_2 is in excellent agreement with the value of 18.2 kcal mol^{-1} predicted by the general PA/NO_2^+ BE correlation reported in [31].

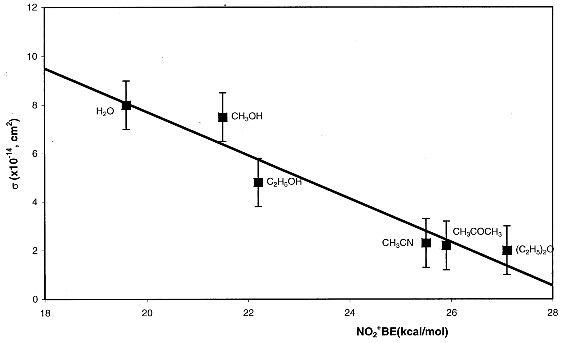

Fig. 2. Calibration plot relating the cross sections σ for the dissociation of L–NO_2^+ species with the NO_2^+ BE of the corresponding ligand L.

3.2.2. Theoretical results

The problems encountered in the experimental measurement of the PA of **1** enhance the interest of an accurate theoretical evaluation of this important thermochemical quantity. As previously mentioned, we have chosen HNO_3, a molecule similar to **1** and well characterized by theoretical and experimental studies, as a model to calibrate the computational results. The PA of HNO_3 calculated at the B3LYP/6-311++g(3*df*,2*pd*) level of theory, 174 kcal mol^{-1} (Table 3) appears to be underestimated, if compared to the 182 ± 2 kcal mol^{-1} experimental value [11a] as well as to a previous high-level result, 182.5 ± 3 kcal mol^{-1} [12].

This suggested to evaluate the PA of **1**, and that of the model HNO_3 molecule, at a higher level of theory. To this end, both the CCSD(T)/cc-pVTZ//B3LYP/6-311++g(3*df*,2*pd*) and the QCISD(T)/6-311+g(3*df*,2*p*), also known as G2, were utilized. From the results summarized in Table 5, the G2 results most closely reproduce the experimental PA of the model HNO_3 molecule, confirming the well documented ability of the G2 approach in calculating thermochemical properties [21]. Accordingly, we regard the G2 PA of HNO_4, 175 ± 2 kcal mol^{-1}, as the most reliable theoretical estimate, in good agreement with the experimental value. In this specific application the CCSD(T) theory leads to PA values of both HNO_3 and HNO_4 somewhat larger than the corresponding experimental values.

Table 5
Coupled cluster electronic energies (CCE) and 298 K enthalpies[a] (CCE298), 298 K G2 enthalpies [G2(298)], coupled cluster (CCPA) and G2 (G2PA) proton affinities,[b] and experimental proton affinities (Expt. PA)

Species	CCE (Hartree)	CCE298 (Hartree)	G2(298) (Hartree)	CCPA (kcal/mol)	G2PA (kcal/mol)	Expt. PA (kcal mol^{-1})
$HONO_2$	−280.519 62	−280.488 76	−280.554 35	184	180	182 ± 2[c]
$H_2ONO_2^+$	−280.822 63	−280.780 31	−280.838 47			
$HOONO_2$	−355.552 58	−355.517 58	−355.598 63	180	175	176 ± 3[d]
$HOOHNO_2^+$	−355.849 86	−355.802 13	−355.874 66			

[a] Thermal corrections are collected in Table 3.

[b] The 5/2RT thermal content of the H^+ at 298 K was also considered.

[c] From [11(a)].

[d] From present study.

4. Conclusions

Despite the severe problems related to the instability of **1**, which prevents its isolation in the pure state and causes extensive decomposition, application of FTICR and MIKE and CAD spectrometry has allowed the gas-phase study of the positive ion chemistry of the acid, in particular as concerns the formation, the structure and the reactivity of $(HNO_4)H^+$ protomers. The mutually supporting evidence from CAD spectrometry and reactive probing by FTICR spectrometry has shown that the ion–neutral $HOOHNO_2^+$ complex (**1a**) is the only protomer formed in CI experiments involving protonation of **1** by H_3O^+ and can be prepared as well upon nitration of H_2O_2. Thermochemically oriented bracketing and kinetic CAD experiments have allowed to evaluate the NO_2^+/H_2O_2 binding energy, 18 ± 2 kcal mol^{-1}, and the proton affinity of **1**, 176 ± 3 kcal mol^{-1}. The theoretical analysis performed at the B3LYP/6-311++g(3*df*,2*pd*), CCSD(T)/cc-pVTZ//B3LYP/6-311++g(3*df*,2*pd*) and QCISD(T)/6-311+g(3*df*,2*p*) (G2) levels of theory has confirmed and extended the experimental picture, showing that indeed the **1a** complex is significantly more stable than the $H_2OONO_2^+$ and $HOONO_2H^+$ protomers, and providing a satisfactory explanation for its exclusive formation in our CI experiments. The G2 approach appears to be the most reliable for the theoretical evaluation of the PA of **1**, giving a value of 175 ± 2 kcal mol^{-1}, in excellent agreement with the experimental value. Formation of protonated peroxynitric acid from the reaction of NO_2^+ with H_2O_2 is a result of potential interest to atmospheric chemistry.

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References

[1] R. Simonaitis, J. Heicklen, J. Phys. Chem. 80 (1976) 1.
[2] A.C. Baldwin, J.R. Barker, D.M. Golden, D.G. Hendry, J. Phys. Chem. 81 (1977) 2483.
[3] C.P. Rinsland, R. Zander, C.B. Farmer, R.H. Norton, L.R. Brown, J.M. Russell, J.H. Park, Geophys. Res. Lett. 13 (1986) 761.
[4] (a) S.Z. Levine, W.M. Uselman, W.H. Chan, J.G. Calvert, J.H. Shaw, Chem. Phys. Lett. 48 (1977) 528; (b) P.L. Hanst, B.W. Gay, Environ. Sci. Technol. 11 (1977) 1105.
[5] (a) R.P. Saxon, B.J. Liu, J. Phys. Chem. 89 (1985) 1227; (b) Z.

Chen, T.P. Hamilton, ibid. 100 (1996) 15734; (c) M.A. Grela, A.J. Colussi, ibid. 100 (1996) 10150; (d) R.D. Bach, P.Y. Ayala, H.B. Schlegel, J. Am. Chem. Soc. 118 (1996) 12758.

[6] Recent studies have pointed out that $HOONO_2$ could be one of those responsible for the athmospherical phenomenon called "chloride deficit by acid displacement." See for example (a) E. Eriksson, Tellus 12 (1960) 63; (b) W.C. Keene, A.A.P. Pszenny, D.J. Jacob, R.A. Duce, J.N. Galloway, J.J. Schultz-Tokos, H. Sievering, J.F. Boatman, Global Biogeochem. Cycles 4 (1990) 407; (c) A.A. Pszenny, W.C. Keene, D.J. Jacob, S. Fan, J.R. Maben, M.P. Zetwo, M. Springer-Young, J.N. Galloway, Geophys. Res. Lett. 20 (1993) 699; (d) B.T. Jobson, H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper, R. Leaitch, J. Geophys. Res. 99 (1994) 25355.

[7] (a) H. Niki, P.D. Maker, C.M. Savage, L.P. Breitenbach, Chem. Phys. Lett. 45 (1977) 564; (b) R.A. Graham, A.M. Winer, J.N. Pitts Jr., ibid. 51 (1977) 215; (c) R.D. Suenram, F.J. Lovas, H.M. Pickett, J. Mol. Spectrosc. 116 (1986) 406; (d) R.D. May, D.B. Peterson, ibid. 150 (1991) 647; (e) T. Zhu, G. Yarwood, H. Niki, Environ. Sci. Technol. 27 (1993) 982; (f) F. Zabel, Z. Phys. Chem. 188 (1995) 119; (g) T. Logager, K. Sehested, J. Phys. Chem. 97 (1993) 10047; (h) T.G. Koch, J.R. Sodeau, ibid. 99 (1995) 10824; (i) J.-M. Regimbal, M. Mozurkewitch, J. Phys. Chem. A 101 (1997) 8822.

[8] For example it is known [7(i)] that the longest lifetime of $HOONO_2$ observed in aqueous solution was as long as 73.9 ± 0.9 min measured in the absence of Cu^{2+} ions (removed by adding Na_2EDTA). In the gas phase the lifetime is much shorter, the lower limit being estimated as long as 12 s at 1 atm and room temperature. However, owing to the very low pressure domain conditions, the lifetime of **1** is expected to be significantly longer in the upper atmosphere.

[9] (a) R.A. Kenley, P.L. Trevor, B.Y. Lan, J. Am. Chem. Soc. 103 (1981) 2203; (b) E.H. Appelman, D.J. Gosztola, Inorg. Chem. 34 (1995), 787.

[10] (a) F. Cacace, M. Speranza, Science 265 (1995) 208; (b) M. Aschi, M. Attinà, F. Cacace, R. Cipollini, F. Pepi, Inorg. Chim. Acta 275–276 (1998) 192.

[11] (a) F. Cacace, M. Attinà, G. de Petris, M. Speranza, J. Am. Chem. Soc. 116 (1994) 6413; (b) G. de Petris, Org. Mass Spectrom. 25 (1990) 83; (c) M. Attinà, F. Cacace, E. Ciliberto, G. de Petris, F. Grandinetti, F. Pepi, A. Ricci, J. Am. Chem. Soc. 115 (1993) 12398; (d) M. Aschi, F. Cacace, G. de Petris, F. Pepi, J. Phys. Chem. 100 (1996) 16522; (e) A. Ricci, Org. Mass Spectrom. 29 (1994) 53.

[12] T.J. Lee, J.E. Rice, J. Am. Chem. Soc. 114 (1992) 8247.

[13] The axial kinetic energy was calibrated by applying a standard procedure as described in the literature: P.H. Dawson, J.B. French, J.A. Buckley, D.J. Douglas, D. Simmons, Org. Mass Spectrom. 17 (1982) 205.

[14] See for example K.L. Bush, G.L. Glish, S.A. McLuckey, MS/MS Techniques and Applications of Tandem Mass Spectrometry, VCH, Weinheim, 1991.

[15] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648; (b) P.J. Stephens, P.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623; (c) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B, 37 (1988) 785.

[16] (a) T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.vR. Schleyer, J. Comput. Chem. 4 (1983) 294; (b) M.J. Frisch, J. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265.

[17] (a) R.J. Bartlett, Annu. Rev. Phys. Chem. 32 (1981) 359; (b) K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.

[18] (a) T.H. Dunning, J. Chem. Phys. 90 (1989) 1007; (b) R.A. Kendall, T.H. Dunning, R.J. Harrison, ibid. 96 (1992) 6796; (c) D.E. Woon, T.H. Dunning, ibid. 98 (1993) 1358.

[19] L.A. Curtiss, K. Raghavachari, G.W. Trucks, J.A. Pople, J. Chem. Phys. 94 (1991) 7221.

[20] D.A. McQuarrie, Statistical Mechanics, Harper and Row, New York, 1976.

[21] For G2, see for example L.A. Curtiss, K. Raghavachari, in Computational Thermochemistry, K. Irikura, D.J. Frurip (Eds.), American Chemical Society Symposium Series 677 American Chemical Society, Washington, DC, 1998. For coupled cluster-based proton affinities, see for example (a) A. Ricca, C. Bauschlicher Jr., Chem. Phys. Lett. 285 (1998) 455; (b) M.E. Pendlum, S. Aloisio, J.S. Francisco, ibid. 285 (1998) 164.

[22] GAUSSIAN 94, Revision D.1, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, L.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.

[23] MOLPRO 96 is a package of ab initio programs written by H.-J. Werner, P.J. Knowles with contributions from J. Almlof, R.D. Amos, M.J.O. Deegan, S.T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A.J. Stone, P.R. Taylor. The closed shell coupled cluster singles and triples program is described in C. Hampel, K. Peterson, H.-J. Werner, Chem. Phys. Lett. 190 (1992) 1.

[24] See for example J.C. Lorquet, in The Structure and Energetic of Organic Ions, T. Baer, C.Y. Ng, I. Powis (Eds.), Wiley, New York, 1996.

[25] (a) Unless stated otherwise, all experimental thermochemical data are taken from S.G. Lias, J.A. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data (1988) 17, Suppl. 1; (b) The proton affinities are taken from the recent compilation, E.P.L. Hunter, S.G. Lias, ibid. 27 (1998) 413.

[26] A list of all the geometrical parameters and harmonic frequencies is available from the authors on request.

[27] This value should be considered as indicative, owing to the fact that the intrinsic effect of the Basis Set Superimposition Error expected to play a significant role, was not taken into account.

[28] B. Asamoto, FT-ICR/MS Analytical Applications of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, VCH, Weinheim, 1991.

[29] G.R. Cooks, J.S. Patrick, T. Kotiaho, S.A. McLukey, Mass Spectrom. Rev. 13 (1994) 287.

[30] L.G. Wright, S.A. McLuckey, R.G. Cooks, Int. J. Mass Spectrom. Ion Phys. 42 (1982) 115.

[31] F. Cacace, G. de Petris, F. Pepi, F. Angelelli, Proc. Natl. Acad. Sci. USA 92 (1995) 8635.