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Original Scientific Paper

On the Proton Affinity of Peroxynitrite and Peroxynitrous Acid

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The proton affinity (PA) of peroxynitrite ($ONOO^-$) and peroxynitrous acid (ONOOH) are calculated to be 1440.5 kJ mol^{-1} and 749.8 kJ mol^{-1}, respectively. Comparison with results for the nitrous, nitric and peroxynitric acid and their anions supports these estimates.

Key words: proton affinity (G2) calculation, dioxonitrate(–), hydrogendioxonitrate, dihydrogendioxonitrate(+), oxoperoxonitrate(–), hydrogenoxoperoxonitrate, dihydrogenoxoperoxonitrate(+), trioxonitrate(–), hydrogentrioxonitrate, dihydrogentrioxonitrate(+), dioxoperoxonitrate(–), hydrogendioxoperoxonitrate, dihydrogendioxoperoxonitrate(+).

INTRODUCTION

Peroxynitrite[#] ($ONOO^-$) is a biological toxin formed by the reaction of nitric oxide with superoxide (O_2^-). Peroxynitrous acid (ONOOH) is formed in the body by protonation (pK_a = 6.8) and yields nitric acid in a fast isomerization reaction.[1–4] The reaction is not of great biological importance

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[#] The compounds according to Ref. 18 have the following names: hydrogenoxoperoxonitrate for peroxynitrous acid, oxoperoxonitrate (–) for peroxynitrite, dihydrogendioxoperoxonitrate(+) for $HOONOH^+$, hydrogendioxonitrate for nitrous acid, dioxonitrate(–) for ONO^-, dihydrogendioxonitrate(+) for $HONOH^+$, hydrogentrioxonitrate for nitric acid, trioxonitrate(–) for NO_3^-, dihydrogentrioxonitrate(+) for HNO_3H^+, hydrogenoxoperoxonitrate for peroxynitric acid, oxoperoxonitrate(–) for O_2NOO^- and dihydrogenoxoperoxonitrate(+) for $HOONO_2H^+$.

because peroxynitrite disappears rapidly *via* reactions with carbon dioxide, thiols and other biomolecules.

It appears that neither peroxynitrite nor peroxynitrous acid have yet been obtained in the gas phase. We have been trying since 1995 to measure the gas phase proton affinity (PA) and other thermodynamic values for peroxynitrite in a Fourier transform mass spectrometer.[5,6] Unfortunately, our attempts were unsuccessful because we were unable to generate gas phase $ONOO^-$ in the spectrometer.[7] However, we obtained an estimate for the PA of $ONOO^-$ and ONOOH from good quality calculations using a standard G2 procedure.[8–11] The recent experimental determination of PA for peroxynitric acid,[12] well supported by experimental results for nitric acid[13–15] and by G2 calculations, makes it worthwhile to compare these results with our own estimates, in which we also use the results of calculations for nitrous acid (HONO) and its conjugate base (NO_2^-).

Thus, our focus will be on the PA of nitrous, nitric, peroxynitrous and peroxynitric acids and their conjugate bases (anions): ONO^-, NO_3^-, $ONOO^-$ and O_2NOO^-. The aim is to deduce the confidence limits for the calculated values.

CALCULATIONS

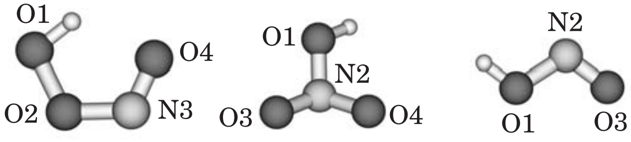
Standard Gaussian-2 (G2 procedure)[8,9] calculations were carried out for the molecular energies. The PA for all compounds, except for peroxynitric acid for which the results of Ref. 12 were used, were calculated employing the equation

$$\mathrm{PA(B_\alpha)} = (\Delta E_{\mathrm{el}})_\alpha + (\Delta \mathrm{ZPVE})_\alpha$$

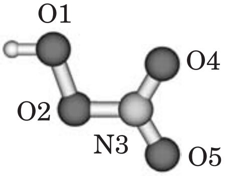
where $(\Delta E_{\mathrm{el}})_\alpha = [E(\mathrm{B}) - E(\mathrm{BH}_\alpha^+)]$ and $(\Delta\mathrm{ZPVE})_\alpha = [\mathrm{ZPVE(B)} - \mathrm{ZPVE}(\mathrm{BH}_\alpha^+)]$ are the electronic and the zero-point vibrational energy contributions to the proton affinity, respectively; B and B^+ denote the base in question and its conjugate acid, respectively; and α represents the site of proton attack. The calculations refer to the *cis*-form: calculations indicate it is the more stable form, and this result is in accord with the available crystal structure for tetramethylammonium peroxynitrite.[16] The PA (G2) of peroxynitrite ($ONOO^-$) and peroxynitrous acid (ONOOH) are calculated to be 1440.5 kJ mol^{-1} and 749.8 kJ mol^{-1}, respectively. The PA (G2) procedure was chosen because it provides the best correspondence to experimental results.

RESULTS AND DISCUSSION

The possibility of proton attachment to various positions (Figure 1), which are indicated in parentheses for the compounds (Table I), yields different ion structures and PA values. The calculated molecular energies of all



Peroxynitrous acid Nitric acid Nitrous acid



Peroxynitric acid

Figure 1. Molecule structure and numbering of atoms in studied acids.

TABLE I

G2 energy and proton affinity of peroxynitrous acid and peroxynitrite

Molecule	E(G2)/a.u.	PA/kJ mol^{-1}
HOONO	–280.509544	no exp value
HOONO + H^+ (O1)	–280.760875	663.2
HOONO + H^+ (O2)	–280.795448	749.8
HOONO + H^+ (N3)	–280.745240	618.4
HOONO + H^+ (O4)	–280.755003	644.8
$ONOO^-$	–279.959670	1440.5
HNO_3	–280.555299	751.4 (exp)
HNO_3 + H^+ (O1)	–280.839416	746.0
HNO_3 + H^+ (O3)	–280.809058	666.1
HNO_3 + H^+ (O4)	–280.793590	625.5
NO_3^-	–280.041719	1348.5
HNO_2	–205.458600	no exp value
HONO + H^+ (O1)	–205.755864	780.3
HONO + H^+ (N2)	–205.695401	621.7
HONO + H^+ (O3)	–205.705608	648.5
NO_2^-	–204.920086	1413.8
$HOONO_2$	–355.593697	736.4 ± 12.6 (exp)
$HOONO_2$ + H^+ (O1)	–355.822623	601.2
$HOONO_2$ + H^+ (O2)	–355.864606	711.3
$HOONO_2$ + H^+ (O4)	–355.845017	659.8
O_2NOO^-	–355.060745	1399.1

these structures (in a.u.) and the corresponding PA values (in kJ mol^{-1}) are given in Table I. As mentioned, the results of the calculations are supported by good agreement with the experimental PA values for nitric (751.4 kJ mol^{-1})[17] and peroxynitric (736.4 kJ mol^{-1})[12] acids. The experimental values for nitric acid and peroxynitric acids provide the opportunity to gauge the confidence with which one can invest the computational results. For nitric acid there is agreement to 5 kJ mol^{-1} and for peroxynitric acid to 25 kJ mol^{-1}. If, in addition, one considers the general performance of the G2 method,[10,11] it would seem that a confidence limit of ± 15 kJ mol^{-1} is fully justified. Thus, if the results are equally valid for nitrous, and particularly for peroxynitrous acid, they indicate that peroxynitrite is the strongest conjugate base, that the PA of peroxynitrous acid is about the same as that of nitric acid, and that it is significantly higher than that for the more related peroxynitric acid.

The results of the calculations also indicate that protonated forms of nitrous and nitric acid prefer the same structure, one in which both hydrogen atoms are attached to the same oxygen atom, whereas in the peroxy acids, the proton prefers the oxygen next to the OH group.

It is interesting to note that Aschi and co-workers[12] did not detect either of the other two less stable protomers of peroxynitric acid, namely $HOONO_2H^+$ and $H_2OONO_2^+$, whose PA's are only 50 and 60 kJ mol^{-1}, respectively, lower than that of the only observed protomer, namely $HOOHNO_2^+$. For nitric acid, both the $H_2ONO_2^+$ and $(HO)_2NO^+$ protomers were observed[12,13] although the calculated difference of 80 kJ mol^{-1} from that of the $(HO)_2NO^+$ protomer is much greater. However, the results did show that the rearrangement to the more stable protomer requires passage over a high activation barrier, which accounts rather neatly for its long life time ($>10^{-5}$ s).[13,14] Consequently, one expects for nitrous and peroxynitrous acids, where the PA difference from the next stable protomer is 130 and 90 kJ mol^{-1}, respectively, that these protomers will not be formed. Calculations also show that protonation of the nitrogen atom in nitric and peroxynitric acid is not possible.

In conclusion, we are still pursuing gas phase experiments on peroxynitrite, and we hope that the present estimate of 1440.5 kJ mol^{-1} for its PA will be confirmed experimentally.

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SAŽETAK

Protonski afinitet peroksinitrita i peroksidušikaste kiseline

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Izračunati protonski afinitet (PA) za peroksinitrit ($ONOO^-$) iznosi 1440.5 kJ mol^{-1}, a za peroksidušikastu kiselinu 749.8 kJ mol^{-1}. Rezultati za dušikastu, dušičnu i peroksidušičnu kiselinu i njihove anione u skladu su s tim vrijednostima.