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Short Communication

Proton affinities of N—O anions and their protonated forms†

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ABSTRACT: The proton affinities (*PA*) of several N—O anions, namely the singly charged anions nitrite, peroxynitrite, nitrate and peroxynitrate and the doubly charged anions *cis*- and *trans*-hyponitrite and oxyhyponitrite, were calculated to be 1413.8, 1440.5, 1348.5, 1414.7, 2065.2, 1987.4 and 1977.9 kJ mol^{-1}, respectively. The *PA* of the corresponding conjugate acids were 780.3, 749.8, 746.0, 724.7, 1394.9, 1448.9 and 1340.7 kJ mol^{-1}, respectively. The *PA* of *cis*- and *trans*-hyponitric and oxyhyponitric acid were 906.7, 723.8 and 728.2 kJ mol^{-1}, respectively. Comparison with the available experimental values for the acids indicates that the calculated values are good estimates of these important quantities. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: proton affinity (G2) calculation; oxonitrate(1-); dioxoperoxonitrate(1-); *cis*- and *trans*-dioxodinitrate(2-); trioxodinitrate(2-); protonated oxonitrate anions

INTRODUCTION

Oxides of nitrogen are of paramount importance in atmospheric and biological chemistry. The gas- and aqueous-phase physico-chemical properties of their various forms have been widely investigated. There also exists an extensive body of chemical data on the gas-phase cations. Much less, however, is known about the thermochemistry of the anions. Several singly or doubly charged N—O anions are known in solution, some of them being rather unstable. Except for nitrate and nitric acid, not much is known about the gas-phase properties of the anions or their corresponding protonated forms (acids). Protonation of these anions produces, at some point, the neutral acid molecules which, in turn, can themselves be protonated. The quantitative definitions of gas-phase acidity (*GA*) and basicity (*GB*) based on such proton transfer (attachment) are

$$\mathrm{AH\ (g)} \rightarrow \mathrm{A^-(g)} + \mathrm{H^+(g)}$$

with

$-\Delta_r G^{\emptyset} = GA$, i.e. the gas-phase acidity of AH

$-\Delta_r H^{\emptyset} = PA$, i.e. the proton affinity of A^-

$$\mathrm{BH^+(g)} \rightarrow \mathrm{B\ (g)} + \mathrm{H^+(g)}$$

with

$\Delta_r G^{\emptyset} = GB$, i.e. the gas-phase basicity of B

$\Delta_r H^{\emptyset} = PA$, i.e. the proton affinity of B

where *PA* is proton affinity. The *PA* values can be determined experimentally by mass spectrometry.[1] One simply monitors whether proton transfer between the species under study and another of known *PA* does or does not occur.

Until recently, small gas-phase molecular dianions with five atoms or less were the province of theoreticians who thought them to be rather exotic hypothetical species.[2,3] Nowadays, more and more reports describe their existence and preparation.[4,5] Our recent *PA* calculations,[6] which showed good agreement with the available experimental data for nitric and peroxynitric acids, inspired us to extend these calculations to some other N—O anions and dianions and their protonated forms (Table 1). We evaluated the relative stability and optimized structures of all the isomers of the protonated substrate, which also gave us a useful insight into the energetics and possible fate of the adducts (i.e. possible fragmentation).

CALCULATIONS

Standard Gaussian-2 (G2 procedure[7,8]) molecular energy calculations for 298 K were performed. The $PA(\alpha)$ values

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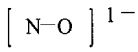
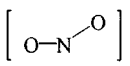
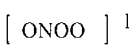
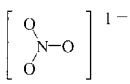
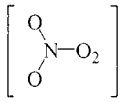
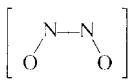
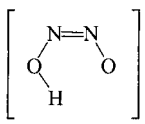
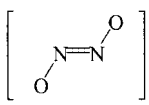
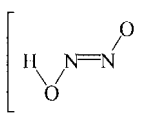
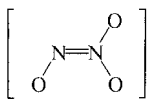
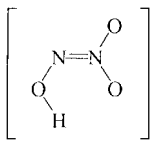
Table 1. N—O anions investigated

Structure	Common name [IUPAC name]	Preparation	Aqueous stability
	Nitroxyl anion [oxonitrate(1-)]	Reduction of NO (chemical or enzymatic)	Dimerizes and converts to N_2O
	Nitrite [dioxonitrate(1-)]	$H_2SO_4 + NaNO_2$ $HCl_{(g)} + NaNO_{2(s)}$	$pK_a = 3.5$, readily disproportionates
	Peroxynitrite [oxoperoxonitrate(1-)]	$O_2^- + NO$ $NaN_3 + O_3$	$pK_a = 6.8$, stable in alkali, $t_{1/2} = 2$ s at room temperature in acid
	Nitrate [trioxonitrate(1-)]	From HNO_3	Stable at all pH
	Peroxynitrate [dioxoperoxonitrate(1-)]	NO_2^+/H_2O_2 or NO_2^-/H_2O_2	$pK_a \approx 5$, decomposes in base
	*cis*-Hyponitrite [*cis*-dioxodinitrate(2-)]	Na reduction of NO in ammonia	Rapidly decomposes to N_2O on exposure to water
	*cis*-Hydrogenhyponitrite [*cis*-hydrogendioxodinitrate(1-)]	Transient	Unstable
	*trans*-Hyponitrite [*trans*-dioxodinitrate(2-)]	Na/Hg reduction of nitrite	Unstable at 4 <pH <14
	*trans*-Hydrogenhyponitrite [*trans*-hydrogendioxodinitrate(1-)]	Transient	Unstable
	Oxyhyponitrite or trioxodinitrate (Angeli's salt) [trioxodinitrate(2-)]	From basic H_2NOH and ethyl nitrate	Unstable at 4 <pH <8
	Hydrogenoxohyponitrite [hydrogen-trioxodinitrate (1-)]	Transient	Unstable

of all compounds, except for peroxynitric acid for which recent results[5] were used, were calculated, where α represents the site of proton attack according to the numbering of atoms in Fig. 1. This particular $PA(\alpha)$ procedure yielding G2 enthalpies for 298 K was chosen because it provides the best correspondence with experimental results.

RESULTS AND DISCUSSION

All the results are presented in Table 2 and Fig. 1. The optimized structures of the most stable forms of the protonated anions and dianions are shown in Fig. 1. For the nitroxyl anion, NO^-, it is the nitrogen atom that is protonated; protonation of all the other anions occurs at the most distant oxygen. However, the most probable site for addition of a proton to these structures is variable. Thus, the possibility of proton attachment to various positions, which for these compounds are indicated in parentheses (Table 2), yields different ion structures and *PA* values. The calculated molecular energies of all structures (in a.u.) and the corresponding *PA* values (in kJ mol^{-1}) are given in Table 2. The experimental values, where available, are also given.

PA of singly and doubly charged anions

The singly charged NO^-, NO_2^-, $ONOO^-$, NO_3^-,

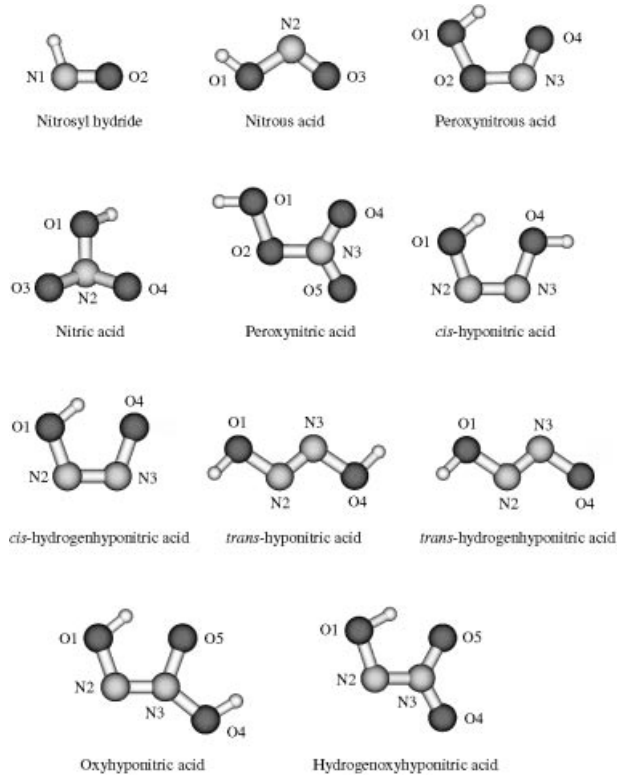


Figure 1. Molecular structure and numbering of atoms in the acids studied

O_2NOO^- and *cis*- and *trans*-$HONNO^-$ and $HONNO_2^-$ differ considerably in their calculated *PA* values and in the position of proton attachment. The structures of their corresponding conjugate acids are shown in Fig. 1. Thus, in $ONOO^-$ and O_2NOO^- protonation occurs at the more distant oxygen of the peroxy group whereas in the others the oxygen closest to the nitrogen is preferred. As mentioned, protonation of the triplet NO^- occurs at the nitrogen atom yielding the singlet HNO; this process exhibits the highest *PA*, 1516 kJ mol^{-1}, of all singly charges ions. The *PA*s of *cis*- and *trans*-$ONNO^{2-}$ are calculated to be 2065 and 1987 kJ mol^{-1}, respectively. The *PA* of $ONNO_2^{2-}$, which protonates at the single oxygen site, is 1978 kJ mol^{-1}. There are no experimental *PA* values with which to make comparison. However, the experimental evidence does support the protonation site suggested by calculations for these compounds.

It is interesting that Aschi *et al.*[10] did not detect either of the other two less stable protomers of peroxynitric acid, namely $HOONO_2H^+$ and $H_2OONO_2^+$, the *PA*s of which 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,[10,11] although the calculated difference of 80 kJ mol^{-1} from that of the $(HO)_2NO^+$ protomer is much greater. However, the nitric acid results[11–13] did show that the rearrangement to the more stable protomer requires passage over a high activation barrier, which accounts rather neatly for its long lifetime ($>10^{-5}$ s).[11,12] 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. Taking the calculated values to be valid and excluding HNO, it follows that *trans*-HONNOH and HOONO are

Table 2. G2 energy and proton affinity of the molecules studied

Molecule (site of attack)	*E*(G2) (a.u.)	*PA* (kJ mol^{-1})
HNO	−130.312563	No exp. value
$HNO + H^+$ (N-1)	−130.576616	693.3
$HNO + H^+$ (O-2)	−130.549476	622.0
NO^-	−129.735151	1516.0
HNO_2	−205.458600	No exp. value
$HONO + H^+$ (O-1)	−205.755864	780.3[6]
$HONO + H^+$ (N-2)	−205.695401	621.7[6]
$HONO + H^+$ (O-3)	−205.705608	648.5[6]
NO_2^-	−204.920086	1413.8[6]
HOONO	−280.509544	No exp. value
$HOONO + H^+$ (O-1)	−280.760875	663.2[6]
$HOONO + H^+$ (O-2)	−280.795448	749.8[6]
$HOONO + H^+$ (N-3)	−280.745240	618.4[6]
$HOONO + H^+$ (O-4)	−280.755003	644.8[6]
$ONOO^-$	−279.959670	1440.5[6]
HNO_3	−280.555299	751.4 (exp.)[9]
$HNO_3 + H^+$ (O-1)	−280.839416	746.0[6]
$HNO_3 + H^+$ (O-3)	−280.809058	666.1[6]
$HNO_3 + H^+$ (O-4)	−280.793590	625.5[6]
NO_3^-	−280.041719	1348.5[6]
$HOONO_2$	−355.599567	736.4 ± 12.6 (exp.)[10]
$HOONO_2 + H^+$ (O-1)	−355.839048	628.7
$HOONO_2 + H^+$ (O-2)	−355.875603	724.7
$HOONO_2 + H^+$ (N-3)	−355.845211	644.9
$HOONO_2 + H^+$ (O-4)	−355.845214	644.9
$HOONO_2 + H^+$ (O-5)	−355.849462	656.1
O_2NOO^-	−355.060745	1414.7
cis-HONNOH	−260.701629	No exp. value
cis-$HONNOH + H^+$ (O-1)	−261.001437	787.1
cis-$HONNOH + H^+$ (N-2)	−260.984966	743.9
cis-$HONNOH + H^+$ (N-3)	−260.971804	709.2
cis-$HONNOH + H^+$ (O-4)	−261.047039	906.7
cis-$HONNO^-$	−260.170340	1394.9
cis-$ONNO^{2-}$	−259.383742	2065.2
trans-HONNOH	−260.697816	No exp. value
trans-$HONNOH + H^+$ (O-1)	−260.956047	677.8
trans-$HONNOH + H^+$ (N-2)	−260.973587	723.8
trans-$HONNO^-$	−260.145954	1448.9
trans-$ONNO^{2-}$	−259.388983	1987.4
$HONNO_2H$	−335.783506	No exp. value
$HONNO_2H + H^+$ (O-1)	−336.031868	652.1
$HONNO_2H + H^+$ (N-2)	−336.060866	728.2
$HONNO_2H + H^+$ (N-3)	−336.055198	713.3
$HONNO_2H + H^+$ (O-4)	−336.047379	692.8
$HONNO_2H + H^+$ (O-5)	−336.055198	713.3
$HONNO_2^-$	−335.272839	1340.7
$ONNO_2^{2-}$	−334.519502	1977.9

the weakest of all of these acids. However, we doubt that *trans*-HONNOH can be prepared. On the other hand, it also follows that the strongest acid is HONNO·OH (Angeli's acid), the *PA* of which of 1341 kJ mol^{-1} is slightly lower than that of HNO_3, 1349 kJ mol^{-1}, followed by that of *cis*-HONNOH, 1395 kJ mol^{-1}. However, the only acid that is actually available in our laboratories is nitric acid.

Structure of the protomers

According to the calculations, proton attachment to the neutral molecule may result in structures that differ considerably from the starting neutrals. Some such cases are the following:

- the H_2ONO^+ protomer of HONO, corresponding to a calculated *PA* of 780.3 kJ mol^{-1}, has the $(H_2O + NO)^+$ structure with an N—O distance of 220 pm;
- the H_2OONO^+ and $(HO{\cdot}OH{\cdot}NO)^+$ protomers of HOONO both have the structure $(H_2O_2 + NO)^+$ with N—O distances of 180 and 220 pm, respectively;
- the $(H_2ONO_2)^+$ protomer of HNO_3 has the structure $(H_2O + NO_2)^+$ with an N—O distance of 240 pm;
- the two protomers $H_2OONO_2^+$ and $HO{\cdot}OH{\cdot}NO_2^+$ have N—O separations of 180 and 250 pm, respectively;
- the two H_2ONNOH^+ protomers of *cis*-HONNOH corresponding to calculated *PA* values of 787.1 and 906.7 kJ mol^{-1} have the structures $H_2O + N_2OH^+$, with an N—O distance of 250 pm, and $N_2O + H_3O^+$, with an O—N distance of 160 pm, respectively;
- protonation of atom O-4 in oxyhyponitric acid (Fig. 1) yields $HONN(OH)_2^+$, which has the structure $(H_2O + ONNOH)^+$ with an N—O distance of 240 pm.

All the other protomers have the structures expected from simple attachment to the corresponding protonation site.

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