Protonation of Nitrous Acid and Formation of the Nitrosating Agent NO^+: an *Ab initio* Study

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The most favourable conformation of nitrous acid HONO have been calculated using STO-3G, 3-21G, and 4-31G basis sets. Protonation is predicted to occur on the hydroxylic oxygen to give (**4**) as the most stable structure. This shows an unusually long N–O(2) bond distance and is best represented as a complex between NO^+ and H_2O since the geometries are only slightly changed from the isolated molecules. Rotation about the N–O(2) bond requires only a few hundred cal mol^{-1} as shown by calculations on the non-planar structures (**7**) and (**8**). The site of protonation can be correctly predicted from both the molecular electrostatic potential of HONO and from a calculation of the spatial extent of the lone pairs on the oxygens. The dissociation energy for $[H_2ONO]^+$ to give NO^+ is calculated as 18.2 kcal mol^{-1} (6.31**//3-21G), consistent with rate-determining nitrosonium formation under some reaction conditions.

The diazonium salts play an important role in synthetic organic chemistry.[1] Their preparation involves several steps initiated by the treatment of a primary amine (RNH_2) with nitrosating agents (XNO). Among the latter nitrous acid (HONO) is the most frequently employed. The kinetics and mechanism of nitrosation by nitrous acid have been the subject of intensive experimental study,[2,3] which has shown that these reactions are dependent upon the acidity of aqueous solutions.

In weakly acidic medium (pH $\geqslant$ 2), the anhydride of nitrous acid (N_2O_3) is found to be the reactive nitrosating agent.[4,5] However the rate-determining step at higher acidity (pH $\leqslant$ 1) involves an attack either by free nitrosonium ion, NO^+, or by its hydrated form, $H_2NO_2^+$.[1]

It appears that an equilibrium is established between both forms [equation (1)], but the equilibrium position is not

$$HNO_2 + H^+ \rightleftharpoons H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \quad (1)$$

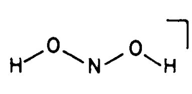
accurately known. In strong acidic solution, there is good evidence for the existence of the nitrosonium ion NO^+ which acts in this region as an active nitrosating agent.[6]

The protonation of HNO_2 has been discussed in previous theoretical papers.[7,8] Dargelos *et al.*[7] carried out an optimization of the geometries of six possible protonated forms of nitrous acid employing the minimal STO-3G basis set. The relative stability of both *cis*- and *trans*-isomers of HNO_2 was calculated but an apparent failure of the molecular electrostatic potential (m.e.p.) to predict the most favourable site of protonation was reported. The most stable protonated species reported was (**1**), obtained from STO-3G-geometry optimization.

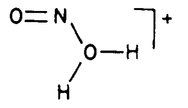
In a subsequent paper, Edwards and Weinstein[8] showed that this apparent failure was due to a basis set effect and the conclusions were reversed in calculations using a larger basis set. Indeed, a good agreement between the m.e.p. predicted and the fully optimized structures for the most stable protonated species (**4**) has been found at 4-31G level. However, these latter authors[8] have performed their 4-31G calculations without geometry optimization, making use of the STO-3G-geometries given by Dargelos *et al.*[7]

It would seem, therefore, of interest to obtain fully optimized geometries for nitrous acids and its various protonated species at an adequate level of calculation in order to determine the most stable structure as a necessary step in understanding the nitrosation reaction.

In this work, we have considered two forms (*cis* and *trans*) of nitrous acid (HNO_2) and their eight possible protonated forms by completely optimizing all geometrical parameters by a gradient method. Furthermore, the m.e.p. and the proton affinity have also been examined.



(1)



(4)

Experimental

Calculations.—Ab initio SCF calculations of structure and properties of various forms have been carried out employing the minimal STO-3G basis set, the split-valence 3-21G and 4-31G basis sets, and the split-valence plus polarization functions 6-31G** basis set of Pople's group.[9–12]

The molecular geometry was optimized by the force-gradient method with analytical gradient[13] as implemented in the MONSTERGAUSS program.[14] The molecular electrostatic potential (m.e.p.) was obtained by means of a modified version of the DENPOT program[15] including the calculations with polarization *d*-functions.

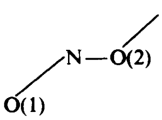
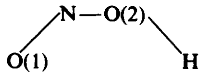
Results and Discussion

(1) *Nitrous Acid* HONO.—The optimized geometries of both *cis*- and *trans*-isomers of nitrous acid calculated using STO-3G, 3-21G, and 4-31G basis sets are summarized in Table 1. Previous *ab initio* and experimental values are also included.

Our STO-3G results are the same as those reported by Dargelos *et al.*[7] The calculated geometric parameters on the whole are in acceptable agreement with the experimental results. The calculated dipole measurements are over-estimated, except for the STO-3G value of the *trans*-isomer, with respect to the experimental values determined by microwave spectroscopy.[18]

The SCF and relative energies using different basis sets are reported in Table 2. The sign of the calculated *cis*–*trans* energy difference (ΔE) is sensitive to the basis set employed, being negative with STO-3G//STO-3G (STO-3G energy

Table 1. Calculated and experimental geometries of *trans*- and *cis*-nitrous acid. Distances in Å and angles in degrees

		STO-3G[a]	3-21G[b]	4-31G[b]	DZ[c]	Exp.[d]
trans						
	r[NO(1)]	1.224	1.179	1.166	1.169	1.169
	r[NO(2)]	1.415	1.442	1.400	1.447	1.442
	r[O(2)H]	0.993	0.969	0.953	0.962	0.959
	$O(1)\hat{N}O(2)$	108.3	110.2	111.4	110.4	110.6
	$N\hat{O}(2)H$	101.5	104.8	107.9	105.2	102.1
	μ	1.68	2.58	2.79	2.50	1.93[e]
cis						
	r[NO(1)]	1.227	1.189	1.177	1.179	1.186
	r[NO(2)]	1.402	1.420	1.377	1.425	1.399
	r[(O(2)H]	1.001	0.978	0.965	0.972	0.989
	$O(1)\hat{N}O(2)$	110.3	112.3	113.9	113.1	113.5
	$N\hat{O}(2)H$	103.9	107.2	111.6	108.5	103.9
	μ	1.51	1.56	1.80	1.59	1.43[e]

[a] Ref. 7. [b] This work. [c] Ref. 16. [d] Ref. 17. [e] Ref. 18.

Table 2. Calculated SCG energies (in a.u.) and energy differences (in kcal mol^{-1}) of *trans*- and *cis*-nitrous acid.

Method	E_t(*trans*)	E_t(*cis*)	ΔE (*trans* − *cis*)[c]
STO-3G//STO-3G[a]	−201.915 59	−201.915 45	−0.09
3-21G//3-21G	−203.466 01	−203.468 50	1.56
4-31G//4-31G	−204.311 91	−204.310 89	−0.64
DZ//DZ[b]	−204.312 13	−204.312 17	0.02
6-31G**//STO-3G	−204.627 57	−204.630 85	2.06
6-31G**//3-21G	−204.636 22	−204.637 83	1.01
6-31G**//4-31G	−204.641 06	−204.642 69	1.02

[a] Ref. 7. [b] Ref. 16. [c] $\Delta E = \Delta E_t(trans) - E_t(cis)$.

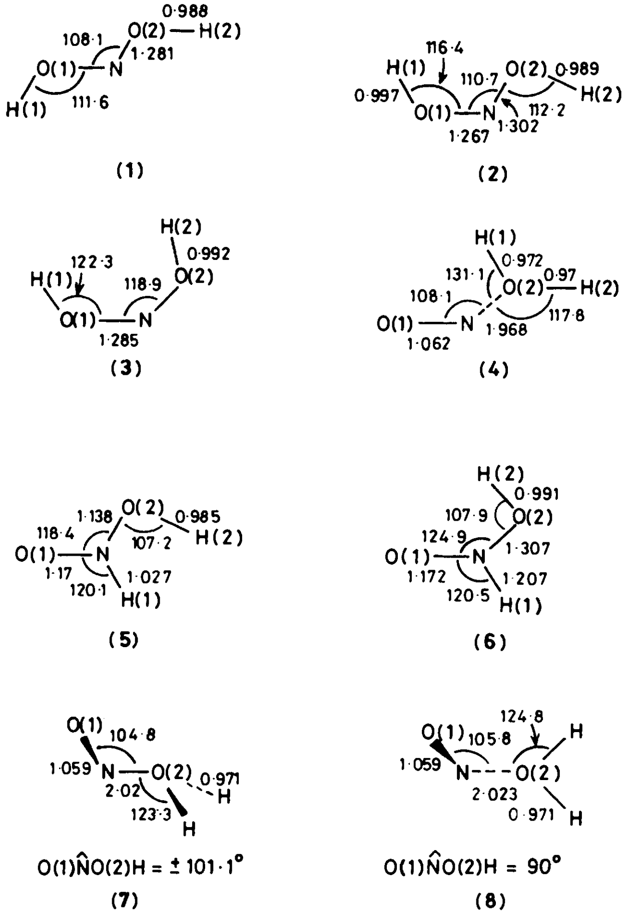


Figure 1. Optimized geometries (3-21G) of eight forms of protonated nitrous acid, $H_2NO_2^+$. Bond lengths in Å and bond angles in degrees

calculated using STO-3G geometry) and 4-31G//4-31G and positive with the remaining ones. However, their absolute values are shown to be negligibly small ($\leqslant$ 2 kcal mol^{-1}).

From the i.r.-induced *cis–trans* isomerization of nitrous acid in solid N_2 and Ar matrices, it is probable that the *trans*-isomer is more stable by *ca.* 0.4 ± 1 kcal mol^{-1} than the *cis*-isomer.[19,20] Because of the precision of the measurements required, the doubt still exists as to the identity of the most stable isomer of the nitrous acid.

It is worth noting that the inclusion of polarization functions always favours the *cis*-isomer, whereas it was previously reported that the correlation effect acts in favour of the *trans*-isomer.[7] Because the energy difference is close to zero, higher levels of calculation including both polarization and correlation effects for fully optimized geometries together with the correction of zero-point energies should be considered in order to produce, quantitatively and with confidence, this small value.

(2) *Protonated Nitrous Acid* $H_2NO_2^+$.—In Figure 1 are shown the six planar protonated forms **(1)**—**(6)** previously considered by Dargelos *et al.*,[7] together with two non-planar forms **(7)** and **(8)**. The optimized geometries of the eight forms studied using the split-valence 3-21G basis set are recorded in Figure 1.

Their total and relative energies at 3-21G//3-21G and 6-31G**//3-21G levels are collected in Table 3. An initial observation that can be made in comparing the results is that the ordering of relative stability is the same in both levels, and shown as follows: **(4)** > **(7)** > **(8)** > **(1)** > **(2)** > **(6)** > **(5)** > **(3)**. The planar form **(4)** is consequently found to be the most stable among protonated species, in contrast to the STO-3G results of Dargelos *et al.*[7] but in agreement with the 4-31G results of Edwards and Weinstein.[8]

In order to verify these data, we have reoptimized the geometry of form **(4)** within STO-3G and 4-31G basis sets (Table 4).

Table 3. Total (a.u.) and relative (kcal mol^{-1}) energies of $H_2NO_2^+$ species. Geometries are given in Figure 1

	Total energy		Relative energy[a]	
Species	3-21G//3-21G	6-31G**//3-21G	3-21G//3-21G	6-31G**//3-21G
(1)	−203.722 40	−204.906 80	−160.8	−169.4
(2)	−203.720 65	−204.901 52	−159.7	−161.1
(3)	−203.693 82	−204.877 40	−142.9	−151.0
(4)	−203.780 28	−204.961 84	−197.1	−204.0
(5)	−203.703 54	−204.882 59	−149.0	−154.2
(6)	−203.715 01	−204.893 29	−156.2	−161.0
(7)	−203.778 50	−204.961 56	−196.0	−203.8
(8)	−203.777 89	−204.961 14	−195.6	−203.5

[a] Relative energy with respect to the *trans*-nitrous acid. See Table 2 for total energies.

Table 4. Calculated geometries of (4) with different basis sets. Distances in Å and angles in degrees

Parameter[a]	STO-3G[b]		3-21G	4-31G
O(1)N	1.185	(1.206)	1.062	1.056
O(2)N	1.570	(1.451)	1.968	2.129
O(2)H(1)	0.992	(1.005)	0.972	0.957
O(2)H(2)	0.989	(1.005	0.970	0.955
O(1)NO(2)	106.9	(107.6)	108.0	106.1
NO(2)H(1)	125.8	(124.3)	131.1	132.1
NO(2)H(2)	118.4	(117.6)	117.8	116.5

[a] See Figure 1 for the numbering of atoms. [b] Values in parentheses are those given by Dargelos *et al.*[7] The corresponding SCF energy is −202.251 91 a.u.

Compared with data given in ref. 7, our STO-3G geometry of (4) is somewhat different: a shorter NO(1) distance (1.185 Å instead of 1.206 Å) and a much longer NO(2) distance (1.57 Å instead of 1.451 Å). The corresponding SCF energy is calculated to be −202.258 34 a.u.; that is lower than the previous values[7] of −202.251 91 a.u. for (5) and −202.254 06 a.u. for (1). Thus (4) is also the most favourable structure, in good agreement with higher levels of calculation.

Dargelos *et al.*[7] were no doubt misled by an incomplete optimization of the unusual NO(2) bond length. As a matter of fact, this bond length increases from 1.57 Å at STO-3G to 1.968 Å at 3-21G and finally to 2.129 Å at 4-31G level.

The structure (4) is in fact a complex between NO^+ and H_2O rather than a normal cation. The geometries of NO^+ and H_2O fragments in (4) are only slightly changed with respect to those of the relevant isolated species.

The non-planar forms of the $(NO^+{\cdot}H_2O)$ complex (7) and (8) lie only a few hundred cal mol^{-1} above the planar (4). The eigenvalues of the matrix of the energy second-derivatives suggest that (8) appears likely to be the transition state between two minima (4) and (7). In all cases, it must be emphasized that the rotation of NO and H_2O fragments around the intermolecular distance N • • • O(2) is quasi-free.

It is noted that the protonation of formic acid (HCOOH), which is isoelectronic with nitrous acid (NOOH), occurs preferentially at the carbonyl oxygen atom rather than at the hydroxy oxygen atom (at 6-31G**//3-21G the difference is 28 kcal mol^{-1}).[21]

In the earlier work,[7,8] the dependence of the molecular electronic potential (m.e.p.) on the basis sets and thereby its ability to predict the protonation sites have also been analysed.

For a comparison, we have performed the m.e.p. of the *trans*-nitrous acid employing the 6-31G** basis set with the 3-21G geometry. The potential map in the molecular plane is shown in Figure 2, and the potential minima are listed in Table 5.

Table 5. Minima of molecular electrostatic potentials of *trans*-nitrous acid with different basis sets (potential given in kcal mol^{-1})

Minimum[a]	STO-3G//STO-3G[b]	4-31G//STO-3G[c]	6-31G**//3-21G[d]
(1)	−33.1	−34.7	−24.5
(2)	−31.9	−32.1	−28.1
(4)	−37.5	−51.1	−36.5
(5)	−36.4	−14.9	−10.4

[a] For the positions of minima, see Figure 2. [b] Ref. 7. [c] Ref. 8. [d] This work.

Table 6. Net charges of *trans*- and *cis*-nitrous acids[a]

	O(1)	N	O(2)	H
trans-HONO				
STO-3G	−0.091	0.095	−0.217	0.213
3-21G	−0.310	0.426	−0.527	0.412
4-31G	−0.287	0.418	−0.569	0.438
6-31G**	−0.254	0.389	−0.501	0.367
cis-HONO				
STO-35	−0.121	0.122	−0.204	0.203
3-21G	−0.358	0.473	−0.515	0.399
4-31G	−0.351	0.490	−0.561	0.422
6-31G**	−0.310	0.445	−0.495	0.360

[a] For the numbering, see Table 1.

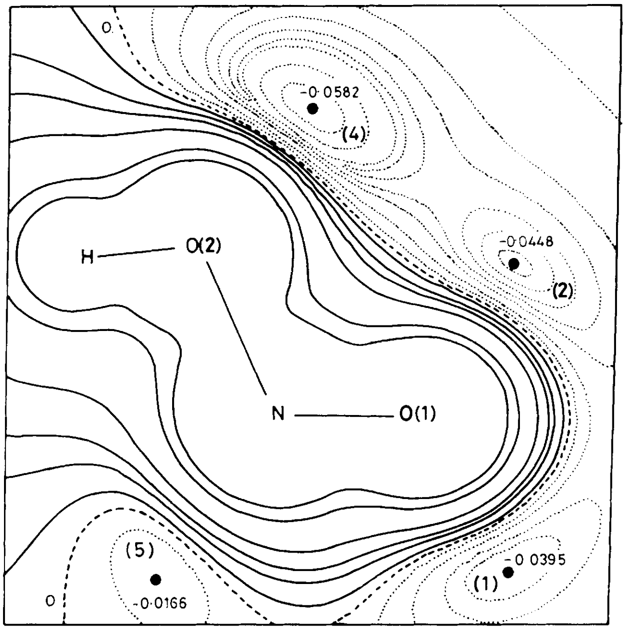


Figure 2. Molecular electrostatic potential (6-31G**//3-21G) in the molecular plane of *trans*-nitrous acid. The isopotential contours have values of 0.5, 0.3, 0.1, 0.05, 0.03, 0.01, 0.0, −0.01, −0.02, −0.03, −0.035, −0.039, −0.042, −0.044, −0.050, −0.055 atomic units. Species (1), (2), (4), and (5) refer to the potential minima and the possible protonation sites

The most interesting feature of Table 5 is although the ordering of potential minima is changed, with basis sets, the deepest minimum in all cases is still found to be that corresponding to (4) (relevant to the lone pair region of the

Table 7. Total and relative energies of (4) and its fragments NO^+ and H_2O in different basis sets

	STO-3G//STO-3G	3-21G//3-21G	4-31G//4-31G	6-31G**//3-21G
H_2O	−74.965 90	−75.585 96	−75.908 64	−76.022 27
NO^+	−127.204 26	−128.137 72	−128.669 67	−128.909 50
$(H_2O + NO^+)$	−202.170 16	−203.723 68	−204.578 31	−204.931 77
(4)[a]	−202.258 34	−203.780 28	−204.626 71	−204.960 84
ΔE[b]	−55.3	−35.5	−30.4	−18.2
PA[c]	215.0	197.1	197.5	203.3

[a] Geometries given in Table 4. [b] $\Delta E = E(4) - E(H_2O + NO^+)$ in kcal mol^{-1}. [c] Proton affinity = E(*trans*-HONO) − E(4)

hydroxylic O(2) atom, see Figure 2). It thus correctly predicts the thermodynamically most favourable site of protonation. These results confirm the conclusions of Edwards and Weinstein.[8]

It is striking to note, on the other hand, the lowest 6-31G** potential minimum of (4) is calculated to be the same as that calculated using STO-3G. The polarization functions have, in some way, cancelled the effect created by an extension of the valence functions. The potential on a nitrogen atom is overestimated by the minimal basis set; it becomes the highest minimum at both 4-31G and 6-31G** levels.

This picture of the electronic distribution can also be emphasized by considering the net charge of the nitrous acid. From Table 6, we note that, in both *cis*- and *trans*-isomers and in all basis sets, both oxygen atoms O(1) and O(2) possess a negative charge with O(2) carrying the largest value. Nitrogen and hydrogen atoms are both positively charged.

Thus for nitrous acid the site of protonation can be correctly predicted by considering the charge distribution alone. However, failures of this prediction method, e.g. with cumulenes, have been reported.[22]

It can be expected that the deeper potential at the lone pair of O(2) is relevant to a larger volume of the electron distribution. As a measure of the spatial extent of the lone pair, we may consider the size (*si*) of the corresponding localized orbital (LMO) of which the definition and the significance have been discussed in a previous work.[23] As a matter of fact, the size of the lone pairs of the O(2) atom $\{si[O(2)]_{LMO}$ 1.36 at 6-31G**//3-21G$\}$ is calculated to be larger than those of the O(1) atom $\{si[O(1)]_{LMO}$ 1.28$\}$ and even larger than those of oxygen atom in the water molecule $[si(O)_{LMO}$ 1.30 at the same basis set].

A quantitative determination of the proton affinity and hence the protonation sites can be made by employing the core-binding energy and the ionization potentials of the molecules. These values are obtained approximately from the energies of the 1*s* and HOMO orbitals energies, respectively. Recently, Catalan *et al.*[24] have proposed relation (2) between the proton

$$PA = 0.306E_{O_{1s}} + 0.5833E_{HOMO} + 182.44 \text{ (in eV)} \quad (2)$$

affinity (PA) at oxygen atoms, on the one hand, and the 1*s* orbital energy of oxygen and HOMO energy of the molecule, on the other hand. Both $E_{O_{1s}}$ and E_{HOMO} are obtained from STO-3G calculations.

If we use the following STO-3G values for the *trans*-nitrous acid, $E[O(1)]_{1s}$ 554.438 eV; $E[O(2)]_{1s}$ 553.558 eV, and E(HOMO) −9.381 eV, we obtain from equation (2) a PA of 169 kcal mol^{-1} at O(1) and of 175 kcal mol^{-1} at O(2).

The most probable site of protonation may thus be predicted again, but the estimated PA[O(2)] is found to be far from the value of 215 kcal mol^{-1} derived from the STO-3G fully optimized structure (4) (see Table 7).

It should be noted that equation (2) was fitted from a multivariate linear correlation on the data of aldehydes and might not be applicable to other types of compounds. The HOMO of nitrous acid does not correspond to the lone pair of the O(2) atom, as found in other series of compounds, but is delocalized on these atoms, with the largest coefficient on O(1). Consequently, the correlation between the proton affinity and the ionization potential alone[25] is invalid in this case.

The calculated PA of 203.3 kcal mol^{-1} (6-31G**//3-21G, see Table 7) is slightly higher than that of 191.7 kcal mol^{-1} calculated for the formic acid at the same level.[24] The latter can be compared with the experimental value of 179 kcal mol^{-1} for formic acid.[26]

(3) *Dissociation of the Protonated Species.*—We are concerned only with (4), since from its dissociation the nitrosating agent NO^+ may be produced [reaction (3)]. the

$$\underset{(4)}{ONOH_2^+} \longrightarrow NO^+ + H_2O \quad (3)$$

total and relative energies of (4) and fragments of interest are given in Table 7. The complex (4) is more stable than its fragments; the energy difference (ΔE in Table 7) between (4) and the sum of energies of both fragments is sensitive to the basis set employed. It decreases as the basis set accuracy increases. Recent work on molecular complexes[27–29] has shown that the correlation effect contributes in an opposite direction to that of polarization effect, but the contribution is quantitatively small. It can therefore be expected that the energy difference (ΔE) amounts, at higher levels of calculation, to a few kcal mol^{-1} larger than the present 6-31G**//3-21G value of ΔE 18.2 kcal mol^{-1}.

Attempts have been made to distinguish between NO^+ and H_2ONO^+ as nitrosating agents in acidic nitrous acid mixtures; under most experimental conditions it is concluded that there is a rapid equilibrium between the two species.[30,31] Thus, for example, Challis has shown that highly reactive substrates react on encounter with nitrous acidium ion (H_2ONO^+), while similar species, best described as solvated NO^+, have been described for reaction in MeOH.[32] Our calculations show that H_2ONO^+ is best represented as a 'hydrated' NO^+ species rather than as a protonated nitrous acid. The dissociation energy of H_2ONO^+ is however calculated to be appreciable (> 18 kcal mol^{-1}), so that the concentration of NO^+ in all but the most highly acidic solution will be very small. The unusual structure of the H_2ONO^+ ion may however result in a relatively small difference in electrophilicity between this and NO^+ and this will be the subject of further study.

Acknowledgements

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