Protonation of Nitric Acid and Formation of NO_2^+. An *Ab initio* Study

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The molecular structures and relative stabilities of nitric acid and its protonated species have been determined by SCF calculations. Protonation takes place preferentially at the hydroxylic oxygen atom, giving a complex of NO_2^+ and H_2O. The dissociation energy [22 kcal mol^{-1} (92 kJ mol^{-1}) at 6-31G**//44-31G level] confirms that the production of NO_2^+ could constitute the rate-determining step in aromatic nitration reactions.

Electrophilic nitration is usually carried out with reagents capable of producing the nitronium ion (NO_2^+). Among a variety of available reagents, a combination of nitric acid (HNO_3) with a second acid, either mineral or organic, such as H_2SO_4 or $MeCO_2H$, is commonly employed. Kinetic evidence for the existence of NO_2^+ as the active nitrating agent has been reported for the nitration of alkylbenzenes.[1,2] Thus the formation of NO_2^+ constitutes the slow step that follows the fast protonation of nitric acid [equations (1)—(3)]. In view of

$$HNO_3 + HA \rightleftharpoons H_2NO_3^+ + A^- \qquad \text{(fast)} \qquad (1)$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O \qquad \text{(slow)} \qquad (2)$$

$$NO_2^+ + C_6H_5R \longrightarrow RC_6H_4NO_2 + H^+ \qquad \text{(fast)} \qquad (3)$$

the importance of these reactions and the scarcity of data on the formation of the nitronium ion, we have performed some SCF calculations on the nitric acid molecule and its protonated species in order to determine the most likely structures which lead to NO_2^+, together with the dissociation energy of the reaction (2).

In the previous paper we have shown that the most favourable protonation site of nitrous acid (HNO_2) is the hydroxylic oxygen atom, foreshadowing the formation of the NO^+ ion.[3]

The geometries of the molecules studied, fully optimized with the split-valence 4-31G basis set [4] and by a gradient method,[5,6] are shown in the Figure. They include two configurations of HNO_3 [planar (**1**) and perpendicular (**2**)], four possible planar forms [(**3**)—(**6**)] and one perpendicular form (**7**) of the protonated HNO_3 [see (**8**)]. The perpendicular forms (**2**) and (**7**) are considered in order to study the rotation of (**1**) and (**6**) around the NO^3 bond.

The Table contains the total SCF and relative energies of these species in both 4-31G//4-31G and 6-31G**//4-31G levels (single point calculations using the polarization functions 6-31G** basis set were carried out on the 4-31G geometries).[7]

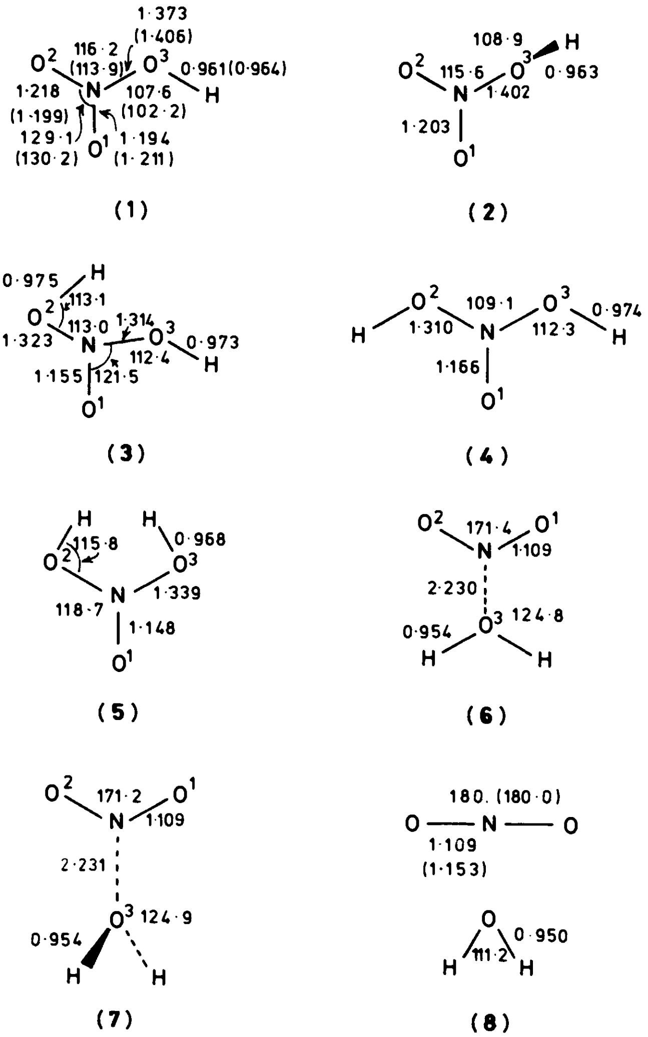

Figure. Optimized geometries (4-31G basis set) of HNO_3, (**1**) and (**2**), $H_2NO_3^+$ (**3**)—(**7**), and NO_2^+ and H_2O (**8**): bond lengths in Å, bond angles in degrees. Values in parentheses are experimental for HNO_3[8] and for NO_2^+[9,10]

Nitric Acid.—In comparison with the available microwave geometry [8] of configuration (**1**) (see Figure), we note an underestimation for the NO^3 bond length in the calculation (0.03 Å). As expected the calculated dipole moments of 3.0 (4-31G) and 2.8 Debye (6-31G**) are both somewhat larger than the experimental value of 2.17 Debye.[8]

The Figure shows that as the O^3H group of HNO_3 rotates, the NO^3 bond tends to lengthen (0.03 Å). The calculated barrier to rotation of 8—9 kcal mol^{-1} (see Table) is consistent with that of 8—12 kcal mol^{-1} determined on the basis of vibrational and calorific measurements.[8] With Koopmans' theorem, the first four vertical ionization potentials of HNO_3 are calculated to be 13.1 (3a″), 14.2 (13a′), 14.9 (12a′), and 15.9 eV (2a″), respectively. These 6-31G**//4-31G values are closer to the lowest bands in the photoelectron spectrum, assigned as 11.95, 12.44, 13.16, and 13.61 ev,[11] than the earlier ones of 13.8, 15.1, 15.2, and 16.6 eV calculated with the double-zeta basis set.[11]

The quadrupole moments are calculated to be (6-31G**//4-31G): $Q_{xx} = -4.68$, $Q_{yy} = 1.02$, and $Q_{zz} = 3.66$ a.u. The calculated electric-field gradients (6-31G**//4-31G) of $q_{xx} = 0.503$, $q_{xx} = -0.405$, and $q_{zz} = -0.097$ a.u. for the nitrogen

Table. Total and relative energies of molecules considered at two levels of calculations

	Total energy/a.u.		Relative energy/kcal mol^{-1} [a]	
	4-31G//4-31G	6-31G**//4-31G	4-31G	6-31G*
(1)	−278.992 11	−279.446 02	0.0	0.0
(2)	−278.980 04	−275.431 26	7.6	9.2
(3)	−279.249 45	−279.719 06	−161.4	−171.3
(4)	−279.247 80	−279.721 02	−160.4	−172.5
(5)	−279.229 16	−279.698 98	−148.7	−158.7
(6)	−279.260 67	−279.733 65	−168.5	−180.4
(7)	−279.258 62	−279.732 06	−167.2	−179.4
NO_2^+	−203.303 91	−203.675 88		
H_2O	−75.908 63	−76.022 69		
(8): $NO_2^+ + H_2O$ [b]	−279.212 54	−279.698 57	−138.3	−158.4

[a] 1 cal = 4.184 J. [b] Sum of energies of NO_2^+ and H_2O.

atom, along with the nuclear quadrupole moment[12] $Q(^{14}N) = 1.56 \times 10^{-26}$ cm^2, allows the nuclear quadrupole coupling constants (eQq) of ^{14}N in nitric acid to be estimated. The values obtained ($eQq_{xx} = 1.75$, $eQq_{yy} = -1.51$, and $eQq_{zz} = -0.33$ MHz, with a rather large asymmetry parameter $\eta = 0.61$) are somewhat larger than the experimental data: $eQq_{aa} = 0.93$, $eQq_{bb} = -0.82$, and $eQq_{cc} = -0.11$ MHz.[13] The absolute values are overestimated, as expected at 6-31G** level, but the relative trend is found to be in good agreement.

The sizes of the localized oxygen lone-pair orbitals[14] (labelled *si*) are of interest, since there appears to be a qualitative correlation between the most favourable site of protonation and the largest volume of electron distribution.[3] The following values are calculated: $si(O^1) = 1.28$, $si(O^2) = 1.29$, and $si(O^3) = 1.34$. Thus it can be expected that the protonation will occur at the O^3 atom.

Protonated Nitric Acid.—From the Table structure **(6)** is the most stable among four planar protonated forms of nitric acid. Like nitrous acid (HNO_2), the protonation site is effectively the hydroxylic (O^3) atom as predicted above. Structure **(6)** is in fact a molecular complex between NO_2^+ and H_2O rather than an ordinary ion. Note that the same structure has been determined for the complex between CO_2 and H_2O both experimentally[15] and theoretically[16] with an intermolecular distance which is significantly larger (> 2.6 Å).[16]

Unlike HNO_2,[3] the energy difference between **(6)** and the remaining forms **(3)** and **(4)** is relatively small ($\leqslant 9$ kcal mol^{-1}). On the other hand, the energy difference between **(6)** and **(7)** (< 1 kcal mol^{-1}) suggests a free motion of both components around N–O^3.

The proton affinity of nitric acid ($HONO_2$: 180 kcal mol^{-1} by 6-31G**//4-31G) is slightly smaller than that of nitrous acid (HONO: 203 kcal mol^{-1} by 6-31G**//3-21G)[3] and approximately equal to that of water (HOH: 179 kcal mol^{-1} by 6-31G**//3-21G).

It is known that the proton affinity, within a homologous series of compounds, is inversely proportional to the first ionization potential.[17] Such a correlation is found in this case. Indeed, the HOMO energies (6-31G**) ordering is calculated as 13.4 (H_2O) > 13.3 (HNO_3) > 12.4 eV (HNO_2). It is emphasized, however, that the HOMO (3a″) of nitric acid is not at all a O^3-predominant orbital. On the contrary, it has 100% *p*-character of the O^1 and O^2 atoms (see also ref. 11). This suggests that the protonation process may not be regarded as an interaction between the proton and the HOMO of the substrate as often reported.[17]

It is also interesting to note a parallel ordering between the size of the protonated oxygen lone pair (*si*) and proton affinity: 1.36 (HNO_2) > 1.34 (HNO_3) > 1.30 (H_2O).

Dissociation of **(6)** *to* NO_2^+ *and* H_2O.—The Table shows that the dissociation energy of **(6)** is 30.2 kcal mol^{-1} at the 4-31G//4-31G level and 22 kcal mol^{-1} at the 6-31G**//4-31G level. The latter value is similar to that of 18 kcal mol^{-1} (6-31G**//3-21G) obtained for the fragmentation of protonated nitrous acid into NO^+ and H_2O. As previously discussed,[3] the correlation effect tends to increase this quantity; thus we can estimate a maximal value of 30 ± 5 kcal mol^{-1} for the separation of **(6)** into its components. Such an appreciable activation barrier could result in the dissociation process **(2)** being rate determining in the electrophilic nitration of reactive aromatic compounds.[1,2,18]

There now appears to be general agreement that nitration by HNO_3 itself or HNO_3 in the presence of mineral acids involves NO_2^+ as the activated nitrating species[19] (although the position in acetic anhydride as solvent is less clear). There is, however, no spectroscopic evidence for the existence of $H_2ONO_2^+$ as a discrete species or indeed as a nitrating agent. The original data showing faster rates of nitration than exchange with the solvent, interpreted in terms of direct nitration by $H_2ONO_2^+$, have been questioned.[19] A somewhat similar situation exists in nitrosation since the rate of reaction with alcohols[20] or H_2O_2[21] which is proportional to [ROH] or [H_2O_2] at low concentration becomes independent of concentration at high [ROH] or [H_2O_2]. This was interpreted originally in terms of slow formation of nitrosating species but more recently it has been concluded that it arises from a medium effect.[22]

An attempt has also been made[23] to measure the rate of reaction of H_2O with NO_2^+. A plot of log k_{obs} against $-\log A_{H_2O}$ is linear with slope −1.95 from which it is concluded that two molecules of water are required to hydrate NO_2^+ (giving H_3O^+ and $HONO_2$ in a concerted step). The calculations presented here show that the –OH group is the preferred site of protonation and that the basicity of this site is little different from that of water itself. There is therefore little driving force for the concerted reaction. The structure **(6)** calculated for 'protonated nitric acid' is akin to a solvated nitronium ion; *i.e.*, major structural reorganization occurs on protonation. Desolvation of this species, because of the large energies involved, could therefore be kinetically significant in solvents of lower acidity.

Because of the similarity between both proton affinity and dissociation energies of nitric acid and nitrous acid, the origin of the difference in the reaction rates of the electrophilic substitution at carbon by NO_2^+ and NO^+ (NO_2^+ undergoes reaction 10^{14} times faster than NO^+)[24] should be examined in the structure of either the NO_2^+ and NO^+ ions or the formation of σ-complexes.

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