

Protonitronium Dication (NO_2H^{2+})¹

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Abstract: Protonitronium dication (**1**, NO_2H^{2+}), the assumed superoelectrophile responsible for the nitration of deactivated aromatics as well as alkanes with nitronium salts in superacidic media, was found to be a minimum at both HF/6-31G* and MP2/6-31G** levels of ab initio calculations. IGLO ¹⁵N NMR chemical shift as well as infrared frequencies were also calculated for **1**. Attempts to experimentally observe **1** under superacidic conditions by ¹⁵N NMR and FT-IR (Raman) spectroscopy were so far unsuccessful, due to the expected low equilibrium concentration of **1** in the studied systems.

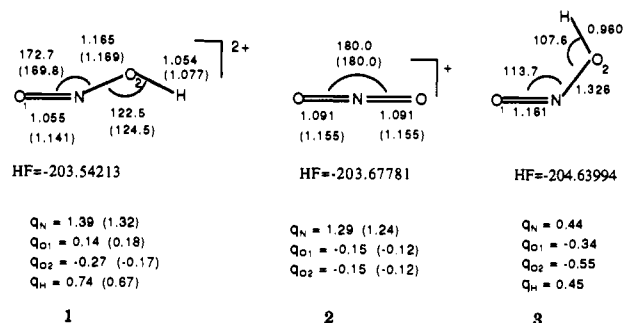
Introduction

Hantzsch's pioneering studies² in the 1930's laid the foundation for Ingold and his associates to establish nitronium ion (NO_2^+) as the reactive electrophile in the acid-catalyzed nitration with nitric acid and its derivatives.³ Olah et al. in 1956^{4a} reported the simple preparation of the remarkably stable nitronium tetrafluoroborate, $\text{NO}_2^+\text{BF}_4^-$, and its use as a convenient and highly efficient nitrating agent. Nitronium salts since gained wide use^{4b} as convenient nitrating agents. They efficiently nitrate most aromatics, but also aliphatic (cycloaliphatic) compounds such as adamantane and diamantane.⁵

Highly deactivated aromatics such as *m*-dinitrobenzene are not nitrated by nitronium salts in aprotic solvents (nitromethane, sulfolane, methylene chloride etc.). However, in superacidic FSO_3H solution, nitronium ion nitrates *m*-dinitrobenzene to 1,3,5-trinitrobenzene.⁶ Similarly whereas nitronium ion shows no reactivity toward methane in aprotic media, it reacts, albeit in low yield, in FSO_3H to give nitromethane.⁷ This indicates that the nitronium ion is activated by the superacidic medium compared to its reactivity in aprotic solvents. To explain the highly increased reactivity of the nitronium ion in strongly acidic medium, we suggested^{7,8} that the nitronium ion could undergo protonation to protonitronium dication (NO_2H^{2+}), **1**, an extremely reactive superoelectrophile. The linear nitronium $\text{O}=\text{N}^+=\text{O}$ is only a polarizable electrophile in its ground state. It has no empty atomic or low-lying LUMO orbital on nitrogen (similar to the ammonium ion), and its electrophilic ability is only due to its polarizability when attracted by π -donor aromatic nucleophiles. In contrast to reactive π -donor aromatics, deactivated aromatics or σ -donor alkanes are weak electron donors and cannot bring about such polarization. A "reactive" nitronium ion should be bent with a developing p-orbital on nitrogen. The driving force for the formation of the bent nitronium ion must be the ability of the oxygen nonbonded electron pairs to coordinate with the strong acid in the nitrating system.

So far no evidence has been obtained for the protonitronium dication **1**. Simonetta's lower level calculation⁹ on the suggested protonitronium dication did not show a minimum. We wish to report now high level ab initio calculations showing the true, intermediate nature of NO_2H^{2+} , as well as IGLO ¹⁵N NMR shift and IR frequency calculations on the dication.

Chart I. Geometries (bond lengths in Å and bond angles in deg), Energies (in hartrees), and Charges at the 6-31G*//6-31G* Level (MP2/6-31G**//MP2/6-31G** level values)



Results and Discussion

Ab initio MO calculations were carried out with the Alliant version of the Gaussian 86¹⁰ series of programs. Initial calculations were performed with the HF/3-21G basis set, and the dication did not converge into a minimum in its singlet state. Subsequent calculations were performed at the HF/6-31G* level, and the ion in fact converged into a minimum. Later we also optimized the ion at the MP2/6-31G** level. Structural parameters along with charge distributions are shown in Scheme I together with data of NO_2^+ (**2**), and neutral HNO_2 (**3**) pertinent to the geometry and charge distribution of NO_2H^{2+} (**1**).

The protonitronium dication (**1**), an analog of nitrous acid (**3**), is characterized by quite shorter $\text{N}-\text{O}_1$ (1.055 Å) and $\text{N}-\text{O}_2$ (1.165 Å) bonds. The shorter $\text{N}-\text{O}_1$ bond distance is caused by the strong interaction of (formally) doubly occupied p_y and p_z orbitals of oxygens with the empty orbitals of the nitrogen atom thereby generating a somewhat triple bond character of $\text{N}-\text{O}_1$, whereas the shorter $\text{N}-\text{O}_2$ bond is due to the interaction of the empty p_y orbital of nitrogen with the occupied p_y orbital of hydroxyl oxygen making somewhat double bond character of the $\text{N}-\text{O}_2$ bond. This interaction also reflects a $\text{O}-\text{N}-\text{O}$ bond angle (173°) of **1** which is much larger than that of (114°) **3**. In other words, lone pair-bond pair repulsion in **3** makes the $\text{O}-\text{N}-\text{O}$ angle closer to the tetrahedral value. The corresponding cis isomer of dication **1** did not show any minimum and converted into the trans form upon optimization at the 6-31G* level, whereas at the same level calculation the corresponding trans isomer of **3** is 1.4 kcal/mol less stable than the cis isomer. No other isomer of **1** was found as the minimum in its singlet state, including the one in which hydrogen bridges two oxygens. This structure was included in the study based on a suggestion of one of the referees.

Furthermore, we also probed a section of the potential energy surface for $\text{O}=\text{N}^+=\text{O}$ (**2**) with H^+ at the 6-31G**//6-31G* level.

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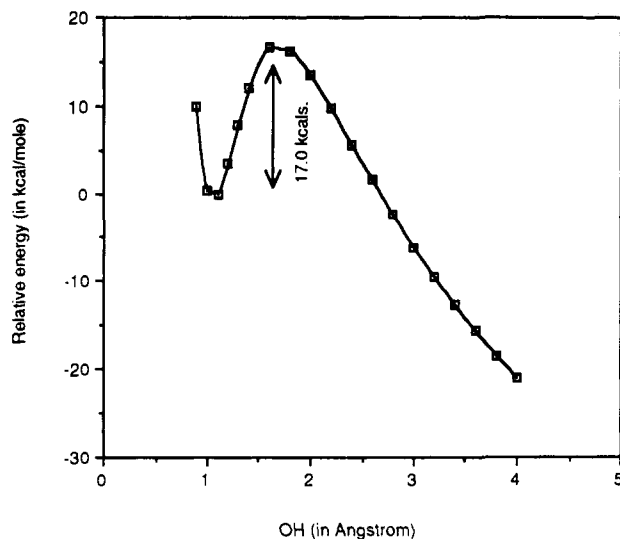


Figure 1. Reaction path of $\text{O}=\text{N}^+=\text{O}$ (**2**) and H^+ (6-31G**//6-31G*). Energy of the optimized NO_2H^{2+} (**1**) is -203.54213 hartrees taken as 0.00 kcal.

Table I. Calculated Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (KM mol^{-1}), and ^{15}N NMR Chemical Shifts^a

compd	HF/6-31G**// HF/6-31G*		MP2/6-31G**// MP2/6-31G**		experiment
	ω	I	ω	I	
1	2760	190	2526	1717	
	2666	1773	2415	19	
	1426	3	1246	2	
	1006	540	884	408	
	682	0	553	21	
	630	50	541	51	
	^{15}N , 272.8 ^b				
2	2654	919	2566	62	
	1682	0	1302	0	
	750	5	601	3	
		^{15}N , 268.3 ^b			^{15}N , 251.0 ^c
HNO_3	^{15}N , 366.8 ^b			^{15}N , 377.0 ^c	

^a Both experimental and calculated ^{15}N NMR chemical shifts are referenced to NH_3 . ^b Calculated at II//6-31G* level. ^c Taken from ref 14.

We chose O-H as the reaction coordinate. The reaction coordinate was scanned in the range 0.9–4.0 Å. For each point we fully optimized the geometry at the 6-31G* level. A plot of the relative energy versus the reaction coordinate is shown in Figure 1. The deprotonation barrier was calculated to be 17.0 kcal/mol. It should be mentioned that the calculated results refer to the gas phase, while in superacidic solvents dications should be more favorable through removal of excess charge by solvation or clustering. The reaction of $\text{O}=\text{N}^+=\text{O}$ and H^+ to give NO_2H^{2+} (**1**) is endothermic by +85.1 kcal/mol¹¹ at the same level.

^{15}N NMR chemical shifts of **1** and **2** were calculated (Table I) with use of IGLO¹² (individual gauge for localized orbitals). Due to presence of nonbonded electrons on nitrogen, ^{15}N NMR chemical shifts are more dependent on solvents and temperature than ^{13}C NMR chemical shifts; consequently, calculated ^{15}N NMR chemical shifts could be expected to differ from experimental values. Schindler's¹³ calculation on ^{15}N NMR chemical shifts, however, showed good agreement between theory and ex-

(11) The endothermic nature can be rationalized by electrostatic repulsive effects. However, reaction of H^+ and NO_2^- to give neutral HNO_2 is as expected exothermic by -358.9 kcal/mol. The high exothermal is due to electrostatic attraction.

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periment. Our calculated ^{15}N NMR chemical shift of nitronium ion **2** at the II//6-31G* level is $\delta(^{15}\text{N})$ 268.3, 17 ppm deshielded from the experimental $\delta(^{15}\text{N})$ 251.0.¹⁴ The ^{15}N NMR chemical shift of the protonitronium dication ($\delta(^{15}\text{N})$ 272.5) calculated at the same level is, however, deshielded from the ^{15}N NMR chemical shift of the nitronium ion by only 4 ppm. On the other hand, the calculated ^{15}N NMR chemical shift of nitric acid is $\delta(^{15}\text{N})$ 366.8, 10 ppm shielded from experimental $\delta(^{15}\text{N})$ 377.0.¹⁴ Attempts to experimentally observe the protonitronium dication (**1**) by ^{15}N NMR spectroscopy using ^{15}N -enriched nitronium ion (98%) in a large excess of $\text{HF}:\text{SbF}_5$ did not indicate any chemical shift change from that of the nitronium ion. The result is not unexpected as the protonitronium dication (**1**) is expected to be present only in low concentration in the superacid system and may undergo fast proton exchange.

We also attempted to use faster IR and Raman spectroscopy to observe **1**. The nitronium ion in excess SbF_5 (containing some HF) solvent did not show any change in the Raman frequencies. Furthermore, no new absorptions were observed in the IR spectrum. Again low concentration of **1** would not be detectable by used methods. Calculated harmonic vibrational frequencies of **1** and **2** at the HF/6-31G**//HF/6-31G* and MP2/6-31G**//MP2/6-31G** levels are reported in Table I.

Conclusion

The stability of intermediates and their reactivity are opposite properties. Reactions with stable nitronium ion salts in superacidic solvents showing highly increased nitrating ability therefore raise the question as to the nature of the de facto nitrating agent in the electrophilic nitration of deactivated aromatics or aliphatics in highly acidic media. While the superacidic media provide "stable ion" conditions, they can also further activate the nitronium ion by further protonation (protosolvation). Our present results substantiate the previous suggestion that the protonitronium dication (NO_2H^{2+}) can be a de facto reagent in the electrophilic nitration reaction in highly acidic media.

Experimental Section

^{15}N -enriched sodium nitrate (98%) was obtained from MSD Isotopes, Canada. The superacids $\text{HF}:\text{SbF}_5$ were prepared from freshly distilled HF and SbF_5 . All manipulations using $\text{HF}:\text{SbF}_5$ were carried out in 5-mm quartz NMR tubes. ^{15}N NMR spectra were obtained on a Varian Associates Model VXR-200 NMR spectrometer equipped with a 5-mm variable-temperature broad-band probe. Raman and IR spectra were obtained on a Nicolet 800 FT IR-Raman instrument.

Solutions of $^{15}\text{NO}_2^+$ in $\text{HF}:\text{SbF}_5$. ^{15}N -enriched NO_2^+ ion was prepared by adding 30 mg of 98% $\text{Na}^{15}\text{NO}_3$ to 0.5 mL of freshly prepared $\text{HF}:\text{SbF}_5$ solution at -20 °C in a 5-mm quartz NMR tube.

IR and Raman Manipulations. Commercial $\text{NO}_2^+\text{BF}_4^-$ (20 mg) was mixed with large excess of SbF_5 (0.5 g containing 1% HF) and the resulting mull was smeared on to a AgBr plate under dry N_2 and analyzed by IR. Raman studies were carried out with the mull in a quartz 5-mm NMR tube.

Method, Basis Set, and Geometry. Geometries of the compounds were optimized at HF/6-31G* and MP2/6-31G** levels by using the Gaussian-86¹⁰ series of programs on an Alliant FX/40 computer. IGLO calculations were performed according to the reported method.¹² Huzinaga¹⁵ Gaussian lobes were used as follows:

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Basis II: N or O: 9s 5p 1d contracted to [51111, 2111, 1]
d exponent: 1.0
H: 5s 1p contracted to [311, 1]
p exponent: 0.70
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