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Dr. Richard S. Miller

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COMPUTATIONAL STUDY OF THE STRUCTURE OF DINITRAMINIC
ACID, $\text{HN}(\text{NO}_2)_2$, AND THE ENERGETICS OF SOME POSSIBLE
DECOMPOSITION STEPS

by

Peter Politzer and Jorge M. Seminario

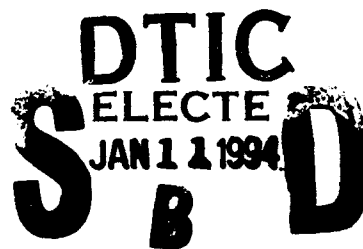
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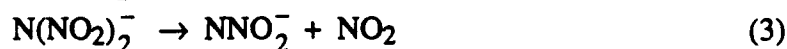
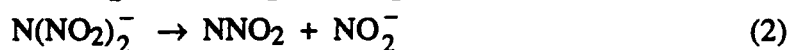
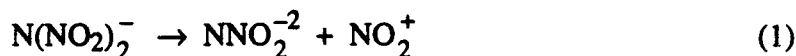
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13. ABSTRACT (Maximum 200 words) MP2/6-31G* geometry optimizations combined with non-local density functional energy calculations were used to determine the structure of dinitraminic acid, $\text{HN}(\text{NO}_2)_2$, and the energetics of several processes that may be involved in its decomposition. These include bond cleavage and also fragmentation induced by protonation.				
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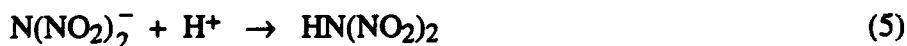
Introduction

The dinitramide anion, $\text{N}(\text{NO}_2)_2^-$, is a new oxide of nitrogen that has recently been prepared and is now known in the form of a number of its salts [1,2]. There is particular interest in the ammonium salt, $\text{NH}_4\text{N}(\text{NO}_2)_2$, as a potentially useful energetic material [1], and there have accordingly been several investigations of its decomposition behavior [1-6]. We have recently completed a computational study of the energetics of some possible decomposition steps of the dinitramide anion [7], in which we used a non-local density functional procedure to determine the energies required for the bond-breaking reactions (1) - (3):



Our conclusion that eq. (3) is the most likely (calculated dissociation energy = 45.5 kcal/mole), followed distantly by eq. (2), is in agreement with observed collision-induced dissociation processes [2].

In the case of ammonium dinitramide, or other dinitramides under acidic conditions, decomposition may involve the initial formation of dinitraminic acid [1,3,4,6]:



Accordingly, our objective in this paper is to examine dinitraminic acid and some of its possible decomposition routes. These include the analogues of eqs. (1) - (3), in which an N- NO_2 bond is broken either homolytically or heterolytically. In addition, acting upon an earlier suggestion [1], we examine the effects of protonating dinitraminic acid, a conceivable mechanism under acid catalysis.

Methods

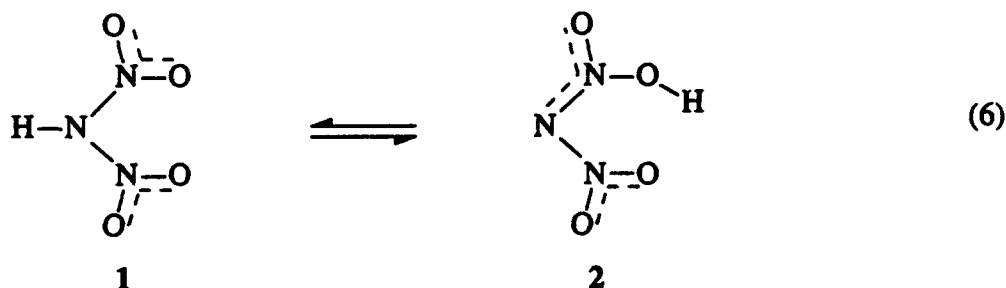
Optimized geometries were computed at the HF/6-31G* and MP2/6-31G* levels for all of the molecules and ions listed in Table 1, using GAUSSIAN 92 [8]. A single-point non-local density functional energy calculation was also carried out in each case with the program *deMon* [9], using the Gaussian DZVPP basis set (which is comparable to the 6-31G**) and the MP2/6-31G* geometry; the exchange-correlation energy was calculated using the generalized gradient approximation (GGA) [10,11]. The effectiveness of non-local density functional methods in computing reaction energetics is well-established [12-16]. All ΔE values presented in this paper

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include corrections for differences in zero-point energies, except where otherwise indicated; these are based on HF/6-31G* vibration frequencies.

Results and Discussion

The first point of interest is whether the hydrogen in dinitraminic acid is on the central nitrogen or on one of the oxygens. As can be seen in Table 1, all three computational approaches agree that the nitrogen is the preferred location for the hydrogen, structure 1. The calculated HF/6-31G* vibration frequencies for 1 show no imaginary values, confirming that it corresponds to an energy minimum. The density functional and the *ab initio* results differ in predicting the order of stabilities among the conformers in which the hydrogen is on an oxygen. The DF-GGA/DZVPP results show 2 to be the most favored among the latter, 3 kcal/mole higher in energy than 1, whereas MP2 calculations, ours and others [17], indicate 3 to be the most stable. (Both 2 and 3 have been shown by the vibration frequency test to be at energy minima [17].) Experimental observations do support the existence of a tautomeric equilibrium [1,2], which we predict to be between 1 and 2, eq. (6). (In evaluating these various results, it should be noted that the total range in energy of the five isomeric forms of dinitraminic acid is only 7.1 kcal/mole at the DF-GGA/DZVPP level and 10.3 kcal/mole at the MP2/6-31G*.)



The MP2/6-31G* optimized geometries of 1 and 2, given in Table 2, are consistent with the structures shown in eq. (6). The O—H distance of 1.581 Å indicates the presence of an internal hydrogen bond in 2.

From the data in Table 1 can be calculated the energies involved in a number of different processes; the results are given in Table 3. Reactions (a) and (b), for which ΔE represents the ionization potential and the negative of the electron affinity of NO_2 , permit comparisons with experimental data; these are also in the table. It is notable that the DF-GGA/DZVPP//MP2/6-31G* values are considerably more accurate than the MP2/6-31G*//MP2/6-31G*, which are 205.8 and -21.4 kcal/mole, respectively. For the heterolytic bond rupture represented by reaction (c), our ΔE is close to the range estimated by Schmitt *et al* for the gas phase ΔH° of deprotonation of dinitraminic acid, between 299 and 310 kcal/mole, based upon observed proton transfer tendencies

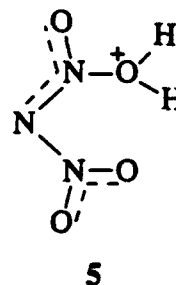
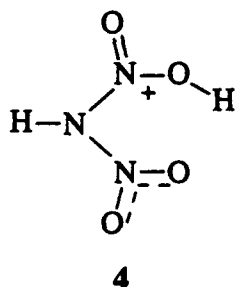
[1,2]. For reaction (d), they infer from the observed failure of $\text{N}(\text{NO}_2)_2^-$ to transfer an electron to several molecules with known electron affinities that $\Delta E > 58.8$ kcal/mole.

Their analysis of reaction (c) led Schmitt *et al* to describe $\text{HN}(\text{NO}_2)_2$ as a very strong gas phase acid [1,2]. Earlier we have reached a similar conclusion for aqueous $\text{HN}(\text{NO}_2)_2$, predicting its pK_a to be -5.6 [18].

In reaction (e), the $\text{H}-\text{N}(\text{NO}_2)_2$ bond is cleaved homolytically. Our computed dissociation energy, 95.8 kcal/mole, seems reasonable in view of the experimental values for the $\text{H}-\text{N}$ bonds in HN_3 , 92 kcal/mole, and N_2H_4 , 87 kcal/mole [19].

Reactions (f) - (h) are the analogues, for dinitraminic acid, of the $\text{N}-\text{N}$ bond breaking reactions shown in eqs. (1) - (3) for the dinitramide anion. The homolytic processes have essentially the same energy requirements; compare eq. (3), 45.5 kcal/mole [7], and reaction (h), 44.0 kcal/mole. (For the latter, Michels and Montgomery have estimated 48 ± 8 kcal/mole [17].) The energies needed for the heterolytic cleavages are all greater, increasing in the order, eq. (2) < reaction (f) < reaction (g) < eq. (1).

More promising as a decomposition route is the protonation of dinitraminic acid, under acid catalysis. Following the suggestion of Schmitt *et al* [1], we examined two possible protonated forms:



At the HF/6-31G* level, we were able to obtain optimized geometries for 4 and a rearranged form of 5 (in which one of the hydrogens had migrated to an oxygen in the other NO_2 group). More important, however, is that we were unable to do so at the MP2/6-31G* level. The inclusion of correlation effects caused both 4 and 5 to come apart; 4 broke up into NO_2^+ and $\text{HN}(\text{NO}_2\text{H})$, and 5 into NO_2^+ , N_2O and H_2O . The fragments obtained from 5 are fully consistent with the decomposition products observed by Schmitt *et al* [1], N_2O and HNO_3 , and this would also be true for 4 if the $\text{HN}(\text{NO}_2\text{H})$ were to break up into N_2O and H_2O . (We find the latter process, $\text{HN}(\text{NO}_2\text{H}) \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$, to be energetically favored; ΔE , without zero-point corrections, is -34.1 kcal/mole.) The net acid-catalyzed decomposition is shown in Table 3 as reaction (i), and is calculated to release 30.2 kcal/mole of energy. This exceeds the energy output for the analogous

decomposition of $\text{N}(\text{NO}_2)_2^-$, eq. (7), by the difference between the protonation energies of NO_3^- [20] and $\text{N}(\text{NO}_2)_2^-$, which is in the neighborhood of 12 kcal/mole.



Summary

We have used non-local density functional theory, in conjunction with MP2/6-31G* geometry optimization, to establish the structure of dinitraminic acid as **1**, in tautomeric equilibrium with **2**, and to compute the energetics of several processes that may be involved in its decomposition. These include the homolytic and heterolytic ruptures of the H-N and N-N bonds. Protonation of dinitraminic acid is shown to lead to its fragmentation in a manner consistent with the observed products of its acid-catalyzed decomposition.

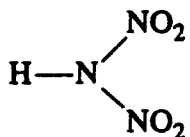
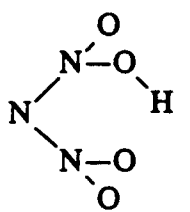
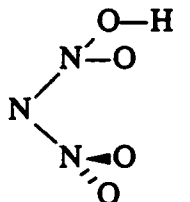
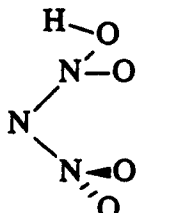
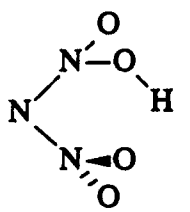
Acknowledgements

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Table 1. Calculated energies.

Molecule or ion	Energy (hartrees)			
	HF/6-31G*//HF/6-31G*	MP2/6-31G*//MP2/6-31G*	DF-GGA/DZVPP//MP2/6-31G*	
	1	-463.05281	-464.30329	-466.12085
	2	-463.03711	-464.28556	-466.11598
	3	-463.03952	-464.29106	-466.11207
		-463.03767	-464.28954	-466.11145
		-463.03377	-464.28690	-466.10957
$\text{N}(\text{NO}_2)_2^-$		-462.54392	-463.78334	-465.60919
$\cdot\text{N}(\text{NO}_2)_2$		-462.44083	-463.64534	-465.45334
$\text{HN}(\text{NO}_2)$		-259.01062	-259.63255	-260.69479
$\text{HN}(\text{NO}_2)^-$		-259.06872	-259.76920	-260.83243
$\text{HN}(\text{NO}_2)^+$		-258.57980	-259.29300	-260.31000

(continued)

Table 1. Calculated energies (continued).

Molecule or ion	Energy (hartrees)		
	HF/6-31G*//HF/6-31G*	MP2/6-31G*//MP2/6-31G*	DF-GGA/DZVPP// MP2/6-31G*
HO-NO ₂	-279.44426	-280.16522	-281.25793
N ₂ O	-183.68012	-184.20414	-184.90574
NO ₂	-204.03149	-204.56420	-205.34645
NO ₂ ⁺	-203.67781	-204.23933	-204.98106
NO ₂ ⁻	-204.06567	-204.59773	-205.41377

Table 2. MP/6-31G* optimized geometries of 1 and 2.

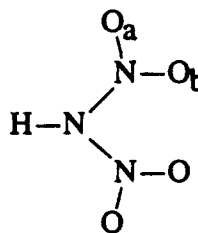
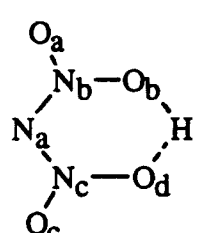
Molecule		Distance (Å)	Angle (deg)
	1	N-N: 1.460 H-N: 1.026 N-O_a: 1.231 N-O_b: 1.222	N-N-N: 115.3 H-N-N: 105.6 N-N-O_a: 112.4 N-N-O_b: 117.8 O-N-O: 129.7
	2	N_a-N_b: 1.322 N_a-N_c: 1.431 N_b-O_a: 1.222 N_b-O_b: 1.362 N_c-O_c: 1.226 N_c-O_d: 1.253 O_b-H: 1.010 O_d...H: 1.581	N_b-N_a-N_c: 117.4 N_a-N_b-O_a: 119.5 N_a-N_b-O_b: 125.3 N_a-N_c-O_c: 111.7 N_a-N_c-O_d: 123.5 O-N_b-O: 115.2 O-N_c-O: 124.8 N_b-O_b-H: 104.4 N_c-O_d-H: 101.3 O...H-O: 148.1

Table 3. Calculated ΔE for various reactions, in kcal/mole.^a

Reaction	ΔE (DF-GGA/DZVPP/MP2/6-31G*)
(a) $\text{NO}_2 \rightarrow \text{NO}_2^+ + \text{e}^-$	+231.2 (+225.7) ^a
(b) $\text{NO}_2 + \text{e}^- \rightarrow \text{NO}_2^-$	-42.6 (-52.4) ^a
(c) $\text{HN}(\text{NO}_2)_2 \rightarrow \text{H}^+ + \text{N}(\text{NO}_2)_2^-$	+312.9
(d) $\text{N}(\text{NO}_2)_2^- \rightarrow \cdot\text{N}(\text{NO}_2)_2 + \text{e}^-$	+96.6
(e) $\text{HN}(\text{NO}_2)_2 \rightarrow \text{H}\cdot + \cdot\text{N}(\text{NO}_2)_2$	+95.8
(f) $\text{HN}(\text{NO}_2)_2 \rightarrow \text{HN}(\text{NO}_2)^- + \text{NO}_2^+$	+192.9 ^b
(g) $\text{HN}(\text{NO}_2)_2 \rightarrow \text{HN}(\text{NO}_2)^+ + \text{NO}_2^-$	+249.2 ^b
(h) $\text{HN}(\text{NO}_2)_2 \rightarrow \text{HN}(\text{NO}_2)\cdot + \cdot\text{NO}_2$	+44.0
(i) $\text{HN}(\text{NO}_2)_2 \rightarrow \text{N}_2\text{O} + \text{HNO}_3$	-30.2

^aExperimental value, taken from ref. 19.^bZero-point energies are not taken into account.