Density functional study of the structure and some decomposition reactions of the dinitramide anion \( \text{N(NO}_2\text{)}_2^- \)

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Abstract

We have used a non-local density functional procedure (DF/GGA/DZVPP) to compute the structure of the dinitramide anion \( \text{N(NO}_2\text{)}_2^- \) and the energetics of some possible decomposition steps. The structures are in good agreement with crystallographic results, and show the \( \text{NO}_2 \) groups to be rotated out of the \( \text{N-N-N} \) plane, with a considerable difference between the two \( \text{N-N-O} \) angles of each \( \text{NO}_2 \) group. Of three possible \( \text{N-N} \) bond breaking reactions, we find that the least energy is required to yield \( \text{NNO}_2^- \) and \( \text{NO}_2 \) (49.8 kcal mol\(^{-1}\)). We suggest that these products have the option of forming a loosely bound complex.

Introduction

Density functional (DF) methods require considerably less CPU time and disk space than ab initio many-body techniques, but do take account of electronic correlation, so they offer a means for investigating the energetics of reactions involving relatively large systems. Even in the local approximation, DF approaches have been effective in predicting activation barriers [1-7], although they suffer from the well-known tendency to considerably overestimate dissociation energies [5,8-11]. This problem can be overcome by using non-local DF methods, or by introducing non-local corrections [5,7,9,12-16].

We have recently carried out a non-local DF analysis of two possible initial steps in the decomposition of nitramide: scission of the \( \text{N-N} \) bond, reaction (1); and nitro-nitrite rearrangement, reaction (2) [16].

We found the \( \text{N-N} \) dissociation energy to be essentially the same as the activation barrier for reaction (2) (48.4 and 48.7 kcal mol\(^{-1}\), respectively), indicating the two processes to be competitive. The same conclusion had been reached earlier by Saxon and Yoshimine on the basis of a multi-reference configuration interaction (MRCISD) study [17], although their calculated energies were approximately 8 kcal mol\(^{-1}\) smaller in magnitude. As a standard for comparison, in the absence of experimental data, we also computed \( \Delta E \) for reaction (1) by the highly accurate G2 procedure [18], which has been shown to be reliable to within 1.6 kcal mol\(^{-1}\), and obtained a value of 53.6 kcal mol\(^{-1}\).

We have now applied non-local DF theory to the investigation of some properties of the dinitramide anion \( \text{N(NO}_2\text{)}_2^- \). Salts of this anion have recently been prepared [19] and are being characterized [20]; it is of considerable interest as a component of new energetic materials. In earlier work, we have estimated the \( pK_a \) of the conjugate acid \( \text{HN(NO}_2\text{)}_2 \).
HzN-NO₂ → H₂N + NO₂

(1)

H₂N-NO₂ → H₂N-NO → H₂N-ONO

(2)

to be −5.6 [21], which would make it a very strong aqueous acid. In this paper we focus primarily upon the energetics of some possible steps in its decomposition.

Methods

Non-local DF calculations, including geometry optimizations, were carried out with the program DEMON [22], using the gaussian DZVPP basis set (approximately equivalent to 6-31G**). The exchange and correlation functionals were formulated in terms of the generalized gradient approximation (GGA) [23,24].

Results

Our optimized structure for N(NO₂)₂⁻ is given in Table 1 and may be compared with crystallographic data for two dinitramide salts, summarized in Table 2. There is generally good agreement between the calculated and experimental structures of N(NO₂)₂⁻, particularly in view of the fact that the latter are for crystalline environments and subject to packing effects, whereas the former is for the isolated anion. In particular, the computed structure shows the observed considerable difference between the two N–N–O angles of each nitro group. This can probably be attributed to steric interference between O₅ and O₇ (Table 1) and the consequent tendencies of these oxygen atoms to move away from each other.

We have investigated the energetics of reactions (3)–(6), all of which have been implicated or proposed on the basis of experimental studies as being involved in the decomposition of the dinitramide anion [25,26].

The results are summarized in Scheme 1. In Table 3 our calculated energy changes for some other reactions involving N(NO₂)₃⁻ and related species are given. We have confirmed by means of the computed vibration frequencies (for structures optimized at the local DF level) that both N(NO₂)₃⁻ and N(NO₂)₄⁺ correspond to energy minima [28].

Discussion

The dinitramide ion can be described in terms of the resonance structures II–IX. Their contributions are far from equal, however. The formal
Table 1
Calculated (non-local DF/GGA/DZVPP) structure of dinitramide anion

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value (Å)</th>
<th>Angle Value (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—N2</td>
<td>1.407</td>
<td>N1—N = N</td>
</tr>
<tr>
<td>N1—N3</td>
<td>1.402</td>
<td>N1—N2—O4</td>
</tr>
<tr>
<td>N2—O5</td>
<td>1.270</td>
<td>N2—N3—O5</td>
</tr>
<tr>
<td>N2—O4</td>
<td>1.262</td>
<td>N2—N3—O7</td>
</tr>
<tr>
<td>N3—O6</td>
<td>1.269</td>
<td>O—N—O</td>
</tr>
<tr>
<td>N3—O7</td>
<td>1.259</td>
<td>N3—N1—N3—O5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N2—N1—N3—O7</td>
</tr>
</tbody>
</table>

Charges suggest that VII–IX are rather unlikely, owing to proximities of strongly negative oxygen atoms, whereas II should be favored. These expectations are supported by both the computed and crystallographic results; in Table 1, the N2—O5 and N3—O7 bonds are shorter than the N2—O4 and N3—O6, and in Table 2, the N—O bonds are shorter than the N—O4.

Our calculations show the two nitro groups in N(NO2)2– to be rotated out of the N—N—N plane by about 27°. This may in part represent a further effort by O5 and O7 to increase their separation; however it may also reflect some delocalization of the two lone pairs on the central nitrogen atom. Assuming that the distribution of the electron pairs around this nitrogen atom is close to tetrahedral (which is supported by the N—N—N angle of 112.4°), then a 27° rotation of the NO2 planes makes them approximately perpendicular to the lone pair orbitals, thereby optimizing conjugation. This is apparently roughly the situation in NH4N(NO2)2, where the N—N—N angle is 113.2° and the two N—N—N—O dihedral angles are 23.8 and 28.3° [29]. In tetraammonium-cubyl dinitramide, in contrast, the N—N—N angles are larger (114.6 and 115.9°) and the N—N—N—O dihedral angles much smaller, ranging in magnitude from 2.9 to 10.5°; indeed, Gilardi has reported that these N(NO2)2− ions are the most planar that he has observed in crystallographic studies of a number of dinitramide salts [29]. In these N(NO2)2− ions, it may be more accurate to regard the two lone pairs on the central nitrogen atom as being in an sp2 orbital in the N—N—N plane and a p orbital perpendicular to it. The latter lone pair could conjugate with both NO2 groups [30].

We have been unable to find a transition state

Table 2
Crystallographically-determined ranges of bond lengths and bond angles in dinitramide anions of ammonium dinitramide and 1,2,4,7-tetraammoniumcubyl dinitramide

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value (Å)</th>
<th>Angle Value (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—N</td>
<td>1.356–1.390</td>
<td>N—N—N</td>
</tr>
<tr>
<td>N—O4</td>
<td>1.227–1.251</td>
<td>N—O4</td>
</tr>
<tr>
<td>N—O5</td>
<td>1.210–1.228</td>
<td>N—O5</td>
</tr>
<tr>
<td>O—N</td>
<td>1.213–123.3</td>
<td>O—N</td>
</tr>
</tbody>
</table>

*Crystallographic data provided by R.D. Gilardi, Naval Research Laboratory.

Table 3
Calculated reaction energetics

<table>
<thead>
<tr>
<th>Process</th>
<th>ΔE (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(NO2)2− + NO2− → N(NO2)3</td>
<td>−151.8</td>
</tr>
<tr>
<td>N(NO2)3 + NO2− → N(NO2)4</td>
<td>−20.8</td>
</tr>
<tr>
<td>N2O → N2O⁺ + e⁻</td>
<td>+299.4 (+297.2)b</td>
</tr>
<tr>
<td>NO2 → NO2⁺ + e⁻</td>
<td>+229.1 (+225.7)b</td>
</tr>
<tr>
<td>NNO2 → N + NO2</td>
<td>+41.9</td>
</tr>
<tr>
<td>NNO2 → N2O + O</td>
<td>+2.1</td>
</tr>
<tr>
<td>NNO2 → N2O⁺ + O⁻</td>
<td>+60.7</td>
</tr>
<tr>
<td>NO2 + O → NO3</td>
<td>−103.2</td>
</tr>
<tr>
<td>NO2 + O⁻ → NO3−</td>
<td>−122.3</td>
</tr>
<tr>
<td>NO2 + e⁻ → NO3−</td>
<td>−62.9 (−52.4)b</td>
</tr>
<tr>
<td>N2O + e⁻ → N2O−</td>
<td>+4.0 (−5.1)b</td>
</tr>
<tr>
<td>NNO2 → N + NO3−</td>
<td>+81.4</td>
</tr>
</tbody>
</table>

* The calculated results do not include zero-point energies.  
  b Ref. 27.
corresponding to that depicted in reaction (6), although under the conditions of Doyle's mass spectrometric studies, an internal rearrangement is believed to be a prerequisite to the formation of the observed NO$_3^-$ [26]. (It should be pointed out, however, that present DF programs are not designed to find transition states.) In this context, it may be relevant to re-examine the supposed transition state in the nitro–nitrite rearrangement of nitramide shown in reaction (2). Although we [16] and Saxon and Yoshimine [17] did obtain an optimized structure with one imaginary frequency for I, its N···N distance is more than twice that in the ground state of H$_2$N–NO$_2$ and the H$_2$N···O distance is actually greater than in the ground state. Saxon and Yoshimine pointed out that the geometries and vibration frequencies of the H$_2$N and NO$_2$ portions of I are very nearly the same as in free NH$_2$I and NO$_2$. Both their and our calculations show the activation barrier to be virtually the same as the N–N dissociation energy. Thus the formation of I can be viewed as equivalent to rupture of the N–N bond followed by a loose association of the NH$_2$ and NO$_2$ fragments. Indeed, we have found subsequently that the NO$_2$ portion of I can undergo rotations at essentially no energetic cost, indicating that the system is on an energy plateau that coincides with the separated NH$_2$, NO$_2$ fragments.

An analogous situation may exist in the case of N(NO$_2$)$_2^-$. The products of the energetically
favored dissociation to NNO₂⁻ and NO₂, shown in reaction (3), may have the option of forming a very loosely-bound complex that can then separate into N₂O and NO⁻. To further examine this possibility, we computed the molecular electrostatic potentials of NNO₂⁻ and NO₂. These show that the most negative regions of NNO₂⁻ are near the oxygen atoms and that a positive potential is associated with the nitrogen atom of NO₂. Thus a very loose electrostatic interaction between the NNO₂⁻ oxygens and the NO₂ nitrogen atom could indeed occur, consistent with Doyle’s interpretation of his experimental results [26].

Summary

We have presented a non-local DF/GGA/DZVPP structure for the dinitramide anion N(NO₂)₂⁻ which is in good agreement with crystallographic results. The considerable difference found between the two N−N−O angles of each NO₂ group is attributed to steric interference between oxygen atoms, which may also be partially responsible for the rotation of the NO₂ groups out of the N−N−N plane; another factor in this rotation may be that it permits increased conjugation between the NO₂ groups and the lone pairs on the central nitrogen atom. We have further found that N(NO₂)₃⁻ and N(NO₂)₄⁺ also correspond to energy minima.

Of three possible N−N bond-breaking reactions that were investigated for the dinitramide anion, the lowest energy requirement (49.8 kcal mol⁻¹) is for the dissociation of N(NO₂)₂⁻ into NNO₂⁻ and NO₂. We suggest that these products have the option of forming a very loose complex, which can subsequently separate into N₂O and NO⁻. We were unable to find a transition state corresponding to an internal rearrangement of N(NO₂)₂⁻.

Acknowledgments

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Olah that we investigate the stability of N(NO₂)₃.
30 The interpretation involving p and sp² lone pair orbitals
is due to Professor J.M. McBride.