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Computational analysis of some possible initial steps in the unimolecular thermal decompositions of 1,3-diazacyclobutane and its 1,3-dinitramine derivative

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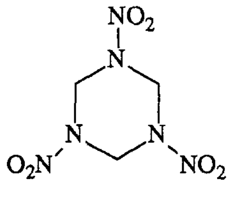
Summary. We have investigated some possible initial steps in the unimolecular thermal decompositions of 1,3-diazacyclobutane and its 1,3-dinitramine derivative, the latter being selected as the simplest example of a symmetric cyclic nitramine. Vibrational analyses were used to identify normal modes that, in the extreme limits, would correspond to bond rupture and molecular decomposition. The energy requirements for ring fragmentation and N–N bond-breaking were computed at the MP4/6-31G* level, using SCF 3-21G optimized structures. It was concluded that ring-fragmentation is a probable initiating step in the decomposition of the unsubstituted molecule, and that it is roughly competitive with N–N bond scission for the dinitramine. The nitro-nitrite rearrangement is predicted, on the basis of SCF calculations, to be less likely than either of the other two processes. It is proposed that N–N bond-breaking may be of primary importance for nitramine stability, but that energetic performance may be determined more by decomposition pathways having energy barriers.

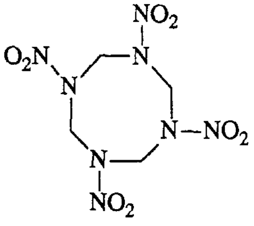
Key words: Nitramines – Vibrational analysis – Thermal decomposition – Activation energies – Dissociation energies

1. Introduction

The elucidation of the thermal decomposition mechanisms of energetic molecules is of considerable importance, both for understanding how the stored energy is released and also for seeking to improve the stabilities of such systems. An important class of energetic molecules are the nitramines, $RR'N\text{-}NO_2$, notable examples of which are 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, I) and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX, II).



I



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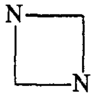

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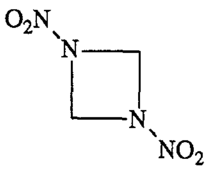


IV

Nitramine decompositions have been extensively investigated [1–14], and considerable attention has focused upon cleavage of the N–NO_2 bond as a key step in the process. This is indeed a rather weak bond, its dissociation energy in various nitramines being estimated as 40–50 kcal/mole [3, 14, 15]. However, there is also evidence of other competing decomposition pathways which may sometimes predominate [2, 5, 6, 10, 13, 14]. For example, laser pyrolysis [13] and quantum chemical [14] investigations of the decompositions of dimethylnitramine and nitramide, respectively, indicate that nitro-nitrite rearrangement is competitive with N–NO_2 bond scission. In the case of RDX (I), it has been inferred from an infrared multiphoton dissociation (IRMPD) study that the main primary decomposition channel is the concerted symmetric ring-fragmentation shown in Eq. (1) [10]:

$$\mathrm{I} \longrightarrow 3H_2C{=}N{-}NO_2 \qquad (1)$$

Other possible mechanisms have also been proposed for the initiation of RDX decomposition [2, 5, 8].

Since the input of thermal energy leads to vibrational excitations within the molecule, it seems reasonable to speculate that unimolecular decay may begin along pathways that are related to normal modes of vibration. Thus, we believe that vibrational analyses may provide insight into the initial portions of the unimolecular decomposition pathways of cyclic nitramines. We have applied this approach to unsubstituted 1,3-diazacyclobutane, III, and its dinitramine derivative, IV. The latter is the simplest analogue of RDX and HMX, I and II.

2. Vibrational analyses

An *ab initio* self-consistent-field procedure, GAUSSIAN 88 [16], was used to compute optimized geometries and the vibrational frequencies and normal modes for III and IV at the 3-21G level. Extensive comparative studies have shown this basis set to be effective for calculating these properties [17]; vibrational frequencies are typically overestimated by 10–15%, but the trends in the experimental values are well reproduced.

1,3-Diazacyclobutane, III, has 24 normal modes of vibration, of which 18 were found to involve primarily the CH_2 and NH groups, while six are associated largely with the ring. These latter are depicted in Fig. 1. Upon examination it is seen that one of these modes, the $1a_2$, can be regarded as supporting molecule dissociation; in the limiting case it would lead to the ring

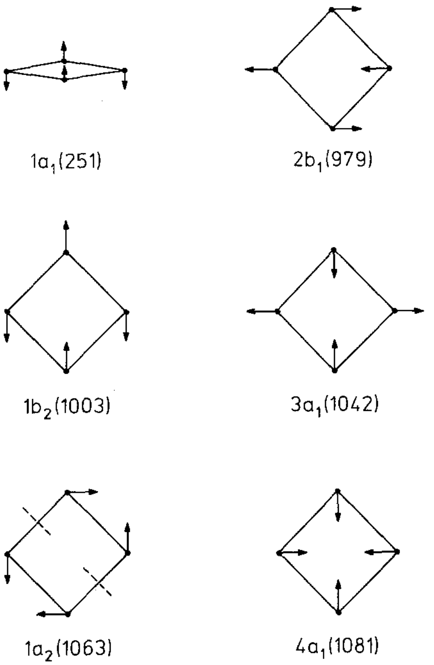
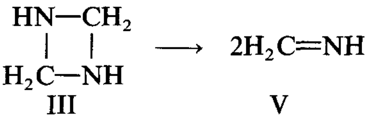


Fig. 1. Calculated normal modes of vibration associated with the ring in 1,3-diazacyclobutane, III. Frequencies, in cm^{-1}, are given in parentheses. The vectors indicate the directions and relative magnitudes of the displacements of the nuclei. The *dashed lines* shown for the $1a_2$ mode identify the bonds that would break in the limit of highly excited vibrations

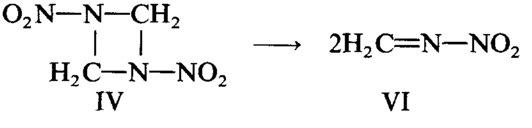
decomposition shown in Eq. (2):



$$\underset{\text{III}}{\begin{array}{c}\text{HN—CH}_2\\ |\quad\ |\\ \text{H}_2\text{C—NH}\end{array}} \longrightarrow \underset{\text{V}}{2\text{H}_2\text{C=NH}} \qquad (2)$$

An additional interesting feature of the $1a_2$ vibrational mode is that it involves a twisting of the CH_2 groups that is consistent with the essentially planar structure of the product V [18]. Since none of the six ring vibrations supports ring-opening through the cleavage of just one bond, we conclude that this is a less probable decomposition mode, even though it cannot, of course, be excluded.

The situation is more complicated for the 1,3-dinitro-1,3-diazacyclobutane, IV. It has 36 vibrational modes, and many of them are rather delocalized, so that they cannot be characterized as involving a specific portion of the molecule. However the two modes that would most clearly support bond rupture and molecular decomposition are found to be relatively well localized, as is shown in Fig. 2; the $4a_2$ is essentially a ring-fragmentation mode, analogous to the $1a_2$ of III, while the $9a_1$ involves a stretching of the N–N bonds. The corresponding bond-breaking processes are indicated in Eqs. (3) and (4):



$$\underset{\text{IV}}{\begin{array}{c}\text{O}_2\text{N—N—CH}_2\\ \quad\ |\quad\ \ |\\ \quad\text{H}_2\text{C—N—NO}_2\end{array}} \longrightarrow \underset{\text{VI}}{2\text{H}_2\text{C=N—NO}_2} \qquad (3)$$

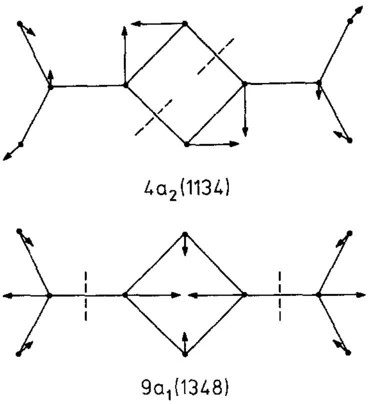
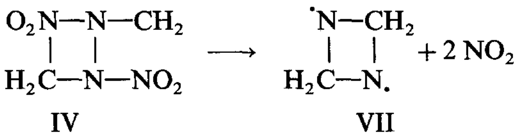


Fig. 2. Calculated normal modes of vibration that most clearly support decomposition of 1,3-dinitro-1,3-diazacyclobutane, IV. Frequencies, in cm^{-1}, are given in parentheses. The vectors indicate the directions and relative magnitudes of the displacements of the nuclei. The *dashed lines* identify the bonds that would break in the limit of highly excited vibrations



$$\begin{array}{c} O_2N{-}N{-}CH_2 \\ |\quad\ | \\ H_2C{-}N{-}NO_2 \\ \text{IV} \end{array} \longrightarrow \begin{array}{c} {}^{\bullet}N{-}CH_2 \\ |\quad\ | \\ H_2C{-}N^{\bullet} \\ \text{VII} \end{array} + 2\,NO_2 \qquad (4)$$

It is interesting to note that the process shown in Eq. (3) is the analogue of the concerted symmetric ring fragmentation that has been proposed as the "dominant primary channel" in the thermal decomposition of RDX [10]. Since Eqs. (2)–(4) can be viewed as depicting the extreme limits of normal vibrational modes of III and IV, we shall investigate these reactions in more detail as possible initiators of the thermal decompositions of III and IV.

3. Energetics of bond-breaking processes

3.1. 1,3-Diazacyclobutane

Ring decomposition in III through the excitation of its $1a_2$ vibrational mode can be analyzed computationally by varying the nuclear positions accordingly. This was accomplished here by choosing the angle α, defined in Fig. 3, to the reaction coordinate. As α decreases, the distances d_1 increase, leading eventually to the products shown in Eq. (2). For each value of α, a complete SCF 3-21G geometry optimization was carried out without imposing any symmetry restrictions, starting always from the geometry corresponding to the previous α. A second series of calculations was performed that consistently started with $\alpha = 20°$, which corresponds approximately to the separated fragments V. (The heavy atoms were restricted to being in the same plane for $\alpha < 50°$.) Both sets of calculations yield virtually the same transition state geometry and potential curve, plotted in Fig. 3. For the maximum of this curve, we performed another vibrational analysis, which yielded exactly one imaginary frequency ($1656\,i\ cm^{-1}$), indicating that the maximum of the potential curve corresponds to a transition state. At the SCF 3-21G computational level, ΔE for the process shown in Eq. (2) is 9.3 kcal/mole, while the activation energy, E_{act}, is 86 kcal/mole. Since SCF values for these energy quantitites are of uncertain reliability [17], we have also calculated the same values at the MP4/6-31G* level, using the 3-21G geometries. ΔE was found to be 2.3 kcal/mole and the activation energy, 76 kcal/mole. Thus, the SCF

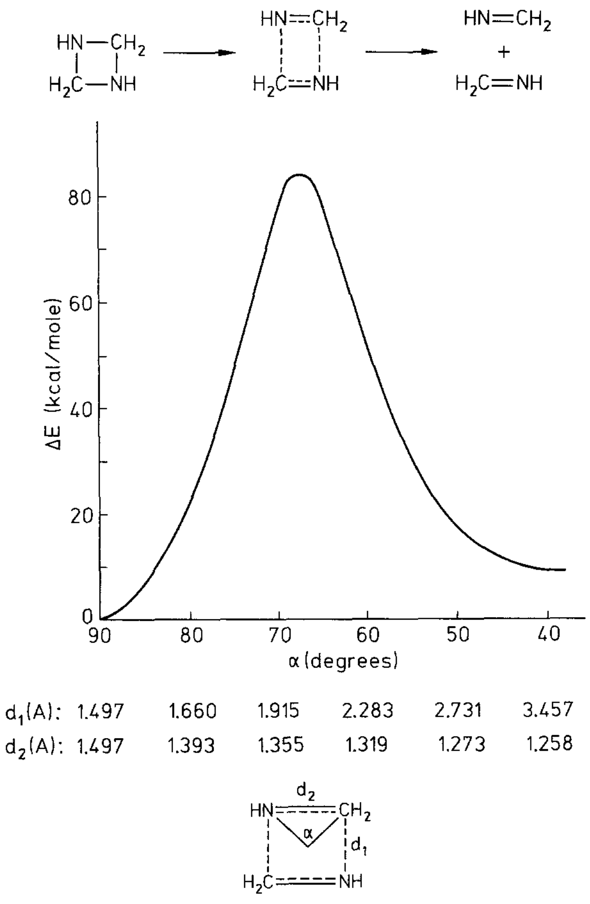


Fig. 3. Potential curve for the ring fragmentation of 1,3-diazacyclobutane, III, as shown in Eq. (2). The reaction coordinate, the angle α, is defined at the bottom of the figure, as are distances d_1 and d_2. Their optimized values are given at 10° increments in α. Structures corresponding to the key points on the potential curve are shown above it

calculation somewhat overestimates these energies, which is typical of what has been observed in a number of other unimolecular dissociations and rearrangements [14, 17, 19, 20]. In any case, these results show that ring fragmentation seems to be energetically possible with respect to the excitation energies accessible with IRMPD techniques [10].

3.2. 1,3-Dinitro-1,3-diazacyclobutane

In view of these results, the question arises as to whether an analogous ring dissociation may be possible in 1,3-dinitro-1,3-diazacyclobutane (IV); this would help to explain the results of the IRMPD study of RDX [10]. Furthermore, we are interested in determining whether such ring dissociation could be competitive with N–N bond-breaking.

The energetics of the ring dissociation process were computed by the same procedure as for III. At the 3-21G level, ΔE is 34 kcal/mole and E_{act} is 71 kcal/mole. The geometrical parameters of the transition state are $d_1 = 2.052$ Å, $d_2 = 1.359$ Å and the N–N distances are 1.429 Å. Repeating the determination of the energy with the 6-31G* basis set and the 3-21G geometry gives $\Delta E = 19$ kcal/mole and $E_{\mathrm{act}} = 74$ kcal/mole. Our results for III, as well as other work [17, 19, 20], suggest that these SCF activation energies for Eq. (3) are probably somewhat too high. We have therefore used the 3-21G structures to compute the MP4/6-31G* activation energy, and indeed find it to be 68 kcal/mole, compared to 76 kcal/mole for III. Thus the presence of the nitro groups slightly destabilizes the ring in this case.

When considering N–N dissociation, it is necessary to recognize that the full course of the gradual transition of the bonded nitro group to the free NO_2 molecule cannot be satisfactorily described by SCF (single determinant) methods, because of the dissociation to open shell fragments and the accompanying extensive electronic rearrangement that takes place [21–23]. Fortunately it is reasonable to assume, on the basis of experimental observations for the N–N bonds in RDX [10] and in agreement with others [3, 14], that Eq. (4) does not proceed through a transition state. Accordingly we computed, at the unrestricted 3-21G SCF level, the structures of only the ground-state molecule and the dissociation products, which we take to be NO_2 (doublet) and the diradical VII (triplet). Using these geometries and the MP4/6-31G* procedure, ΔE for Eq. (4) is 91 kcal/mole. We felt that it would be useful to also calculate the analogous energy requirement for breaking just one of the N–N bonds; this was found to be 51 kcal/mole.

As a test of this approach to treating the dissociation of nitro derivatives, we applied it to nitromethane undergoing C–N bond-breaking as described by Eq. (5):

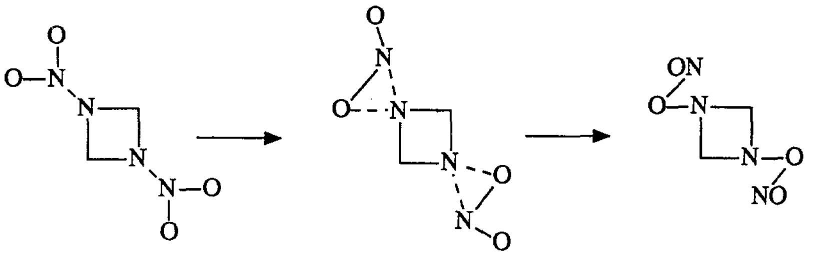
$$H_3C{-}NO_2 \longrightarrow H_3C\cdot + \cdot NO_2 \qquad (5)$$

Using 3-21G unrestricted SCF geometries, the MP4/6-31G* ΔE for Eq. (5) is 62 kcal/mole, in good agreement with the experimentally determined value of 60 kcal/mole [22, 24].

Our analysis indicates that the energy requirement for Eq. (3) is less than for Eq. (4), even though the former is symmetry-forbidden according to the Woodward–Hoffman rules. (In contrast, Eq. (1) is symmetry-allowed, but is believed to have a sizable activation energy [10].) We conclude that the energy actually required for N–N bond rupture due to thermal excitation is likely to range between 51 and 91 kcal/mole, depending upon the extent to which the energy provided is delocalized between the two bonds. Accordingly, for IV, N–N cleavage may be roughly competitive with ring dissociation. It should be pointed out that since the ring decomposition represented by Eq. (3) involves an energy barrier, the possibility of tunneling exists [25], which would further reduce the energy requirement for this process. However the probability of tunneling should be very low if there is an alternative, classically allowed decomposition pathway, e.g. breaking just one N–N bond.

4. Discussion

The results presented so far have focused upon processes that directly involve molecular decomposition. However it seemed appropriate to also look at the nitro-nitrite rearrangement of IV that is presented in Eq. (6):



IV VIII IX (6)

As mentioned earlier, an analogous rearrangement is believed to play an important role in the thermal decompositions of dimethylnitramine [13] and nitramide [14]. Furthermore, our vibrational analysis of IV reveals that the $3a_2$ mode (Fig. 4), which can be viewed as supporting such a rearrangement, has a frequency that is roughly half of the $4a_2$ (ring-fragmentation) frequency (taking into account the 10–15% uncertainty in the calculated values). Thus there is the possibility of Fermi resonance and accordingly strong coupling between these two modes.

For these reasons, we have computed a potential curve for Eq. (6), using the angle β (defined in Fig. 4) as the reaction coordinate and applying the same SCF 3-21G approach as for Eqs. (2) and (3). We found the SCF ΔE for Eq. (6) to be 11 kcal/mole, while $E_{\text{act}} = 167$ kcal/mole. Assuming that the latter value is 15–20% too high (see Sect. 3.2), we arrive at an estimate of about 140 kcal/mole for

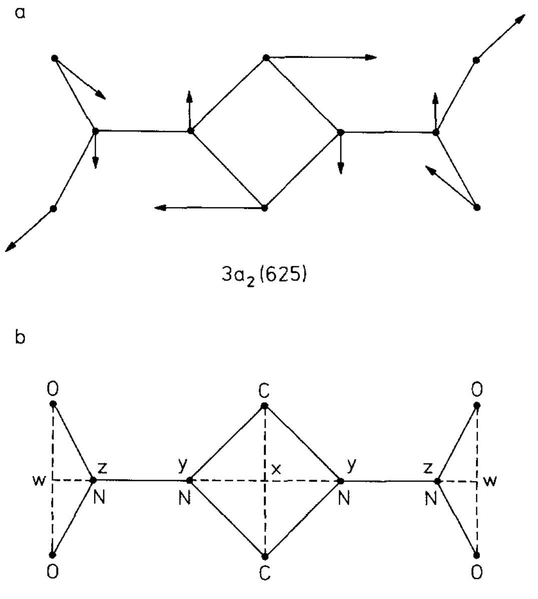


Fig. 4. a Calculated normal mode of vibration that most clearly supports nitro-nitrite rearrangement in 1,3-dinitro-1,3-diazacyclobutane, IV, as shown in Eq. (6). The frequency, in cm^{-1}, is given in parentheses. The vectors indicate the directions and relative magnitudes of the displacements of the nuclei. **b** In computing the potential curve for the nitro-nitrite rearrangement, Eq. (6), each NO_2 group was rotated around an axis through the point *w* and perpendicular to the O–N–O plane. The reaction coordinate was the angle, β, formed by the extensions of the lines *xy* and *zw*. $\beta = 0$ corresponds to the ground state of 1,3-dinitro-1,3-diazacyclobutane (IV). The maximum of the potential curve, structure VIII, occurred at $\beta = 57°$, and the product, IX, corresponds to $\beta = 67°$

E_{act}. While the approximations that were made in obtaining this value clearly introduce a degree of uncertainty, it is sufficiently higher than the energy requirement for either ring fragmentation or N–N dissociation to permit us to suggest that this rearrangement is the least likely of the three processes. It should be mentioned, however, that this conclusion does not exclude the possibility of N–N bond rupture followed by recombination to give the nitrite IX, as could occur in dense phases (liquid or solid).

An interesting aspect of our analysis is the fact that of the two 1,3-dinitro-1,3-diazacyclobutane decomposition processes, Eqs. (3) and (4), only the ring fragmentation involves an energy barrier. This means that some of the energy required to initiate the latter will subsequently be released and could be used to stimulate further decomposition steps. Thus it may be that the thermal stability and shock and/or impact sensitivity of the molecule are determined primarily by the N–N bond rupture [26], while its energetic performance may depend upon decomposition channels with energy barriers. This suggests that if the N–N bonds could be strengthened without significantly affecting the energy barriers of other channels, then it might be possible to diminish sensitivity without major impairment of energetic performance. Such N–N strengthening can result, for example, from a decrease in the pyramidal character of the aza nitrogen and the accompanying increase in the delocalization of its lone pair [27]. Finally, it is important to recognize that since various possible decomposition pathways, with differing energy requirements, do exist for nitramines, the correct interpretation and prediction of the behavior of these systems requires that the amounts of energy supplied to the molecules be accurately known.

5. Conclusions

The analysis of vibrational modes and energetics that has been presented has led us to the conclusion that ring fragmentation is roughly competitive with N–N bond-breaking as an initial step in the thermal decomposition of dinitrodiazacyclobutane, IV. The nitro-nitrite rearrangement is expected to be less likely than either of these processes. For the unsubstituted system, III, ring fragmentation is predicted to initiate decomposition. It is also suggested that the strength of the N–N bond may be a key factor in nitramine stability, whereas energetic performance may depend more upon decomposition pathways that have energy barriers.

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