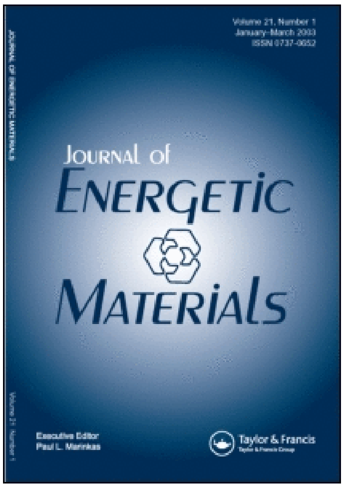

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Thermal decomposition of RDX: A critical review

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To cite this Article Cook, M. D.(1987) 'Thermal decomposition of RDX: A critical review', Journal of Energetic Materials, 5: 3, 257 — 266
To link to this Article: DOI: 10.1080/07370658708012354
URL: http://dx.doi.org/10.1080/07370658708012354

THERMAL DECOMPOSITION OF RDX: A CRITICAL REVIEW

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ABSTRACT

A critical assessment is given of the likely modes of thermal decomposition of RDX. Previous publications by other authors report that thermally decomposed RDX produces nitroxide and nitronylnitroxide radicals as intermediates. These results are discussed, and it is suggested that these radicals are not primary decomposition products, but are formed by the reaction of the radical products of thermal decomposition with molecular oxygen.

Journal of Energetic Materials vol. 5, 257-266 (1987)

Published in 1987 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

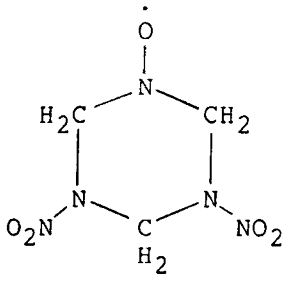
There is much interest at present in elucidating the decomposition mechanisms of energetic materials appropriate to either thermally or mechanically (eg. a shock wave) initiated reaction. It is likely that either a thermal stimulus or a shock wave passed into an energetic material, which causes it to ignite, will involve the same decomposition mechanisms at least in the early stages, provided that pressure effects are not too important. Hence, a study of the thermal decomposition of energetic materials can give valuable information on the chemistry that might be occurring during explosive decomposition.

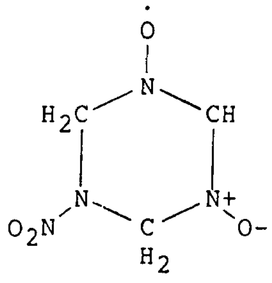
A number of workers [1] and refs therein, have reported that they have detected free radical intermediates, namely nitroxide and nitronylnitroxide radicals, by e.s.r. spectroscopy during the thermal decomposition of RDX in the cavity of the instrument. Whilst this is a very valuable technique for studying the intermediates produced in such decomposition reactions, care must be exercised when interpreting the results. An alternative method of studying the decomposition of energetic materials has been demonstrated by Tang et. al. [2], who used laser irradiation to obtain the high temperatures required and a mass spectrometer to analyse the decomposition products. In this work no structures consistent with either nitroxide or nitronylnitroxide radicals were detected, but their results gave products and reaction schemes that seem very plausible. In this paper we discuss these apparent differences.

THE THERMAL DECOMPOSITION OF RDX

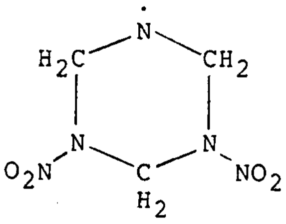
In a recent publication, Pace [1] reported that the thermal decomposition of RDX in the cavity of an e.s.r. spectrometer, produced a spectrum which he assigned to a nitroxide radical [1]. The e.s.r. spectrum obtained during liquefaction of RDX at 200°C was assigned to the nitronylnitroxide radical $(R(N^{+}-O^{-})NO.)$ [2].

This assignment was supported by spectral data from isotopically labelled RDX (RDX-d_6 and RDX-$^{15}NO_2$). It was suggested that the nitroxide radical was formed by loss of NO and the nitronylnitroxide radical by further loss of HNO.

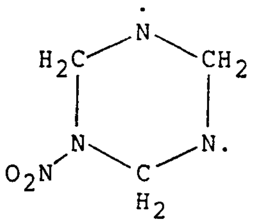

[1]


[2]

These results seem somewhat surprising, since simple considerations suggest that the weakest bond in RDX is the N-N bond of the nitramine group. Thus, on a simple level, the initial decomposition step of RDX must be cleavage of the N-N nitramine bond to form NO_2 and the cyclic aminyl radical [3]. It has been illustrated previously by Brand et. al.[3], that care must be exercised when studying nitrogen containing radicals since reaction of the parent compound or product radical with molecular oxygen can lead to erroneous results. For example, nitroxides can be formed from the reaction of oxygen with aminyl radicals. It would appear therefore, that the most likely route to the formation of the nitroxide radical reported by Pace involves thermal decomposition of a RDX molecule to the cyclic aminyl radical [3], followed by reaction with gaseous oxygen to yield the nitroxide radical [1]. Similarly, the nitronylnitroxide radical probably originates from loss of two nitro groups from a RDX molecule resulting in the diaminyl radical [4]. Reaction with oxygen present only in small quantities would most likely give the nitroxide [5], which by loss of a hydrogen atom would result in a similar structure to [2]. Indeed, deuterium isotope effects have shown a primary effect on the rate of decomposition of liquid RDX, hence it appears C-H rupture must be an important step. The resulting structure [2], should be stabilised by resonance, and this would also assist the loss of a hydrogen atom.

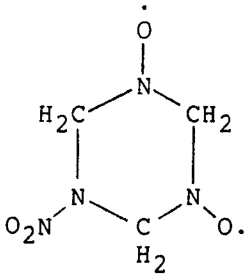


[3]



[4]

The above comments on the thermal decomposition of RDX are supported by the work of Tang et al., who have carried out experiments using a system called LIMA, an acronym for "laser ionisation mass analyser". This apparatus employs a laser pulse to produce ionised species which are then rapidly analysed by a mass spectrometer. The



[5]

ystem allows high temperatures and pressures to be chieved in nanoseconds. Using this technique, Tang et al. have been able to deduce three plausible decomposition schemes outlined in figure 1. It is noticeable that while none of the schemes are consistent with the involvement of nitroxide or nitronylnitroxide radicals, they do indicate the importance of the aminyl radicals [3] and [4]. The decomposition scheme outlined in figure 1a shows successive loss of all three nitrogroups followed by cleavage of two C-N bonds of the ring to give two products of equal mass. The second decomposition scheme, shown in figure 1b, shows loss of two nitrogroups followed by loss of the two oxygen atoms of the remaining nitrogroup. The third decomposition scheme, shown in figure 1c, shows cleavage of two C-N bonds of the ring to give two fragments as the first step. Of the schemes described, the most likely, in our view, is the first. However, the possible involvement of the others cannot be ruled out. It must be borne in mind though, that this technique involves not only high temperatures, but also high pressures and it is possible that the materials under study are being subjected to slightly different conditions from those that exist when the material is undergoing detonation. Furthermore, although the technique is undoubtably fast, the spectra recorded still represent the products which existed after about a microsecond, which still allows plenty of time for further chemical reactions to take place. Despite these minor criticsms, the technique has already contributed to the understanding of detonation chemistry, and further studies can only add to our knowledge.

Discussion

In this paper we have aimed to discuss the current experimental evidence of the thermal decomposition mechanism of RDX. There appears to be two apparently conflicting series of experiments, one group of workers imply that nitroxide radicals are produced directly from thermolysis of RDX, whilst it is clear from another groups work that this is not the case. We have examined these findings taking into account simple theoretical considerations and have aimed to show that the primary step in the thermal decomposition of RDX must involve loss of NO_2 to form initially, an aminyl and then subsequently a diaminyl radical. The nitroxide radicals observed by e.s.r. spectroscopy by Pace can then be accounted for by oxidation of these aminyl radicals by gaseous oxygen.

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FIGURE 1

Figure 1(a)

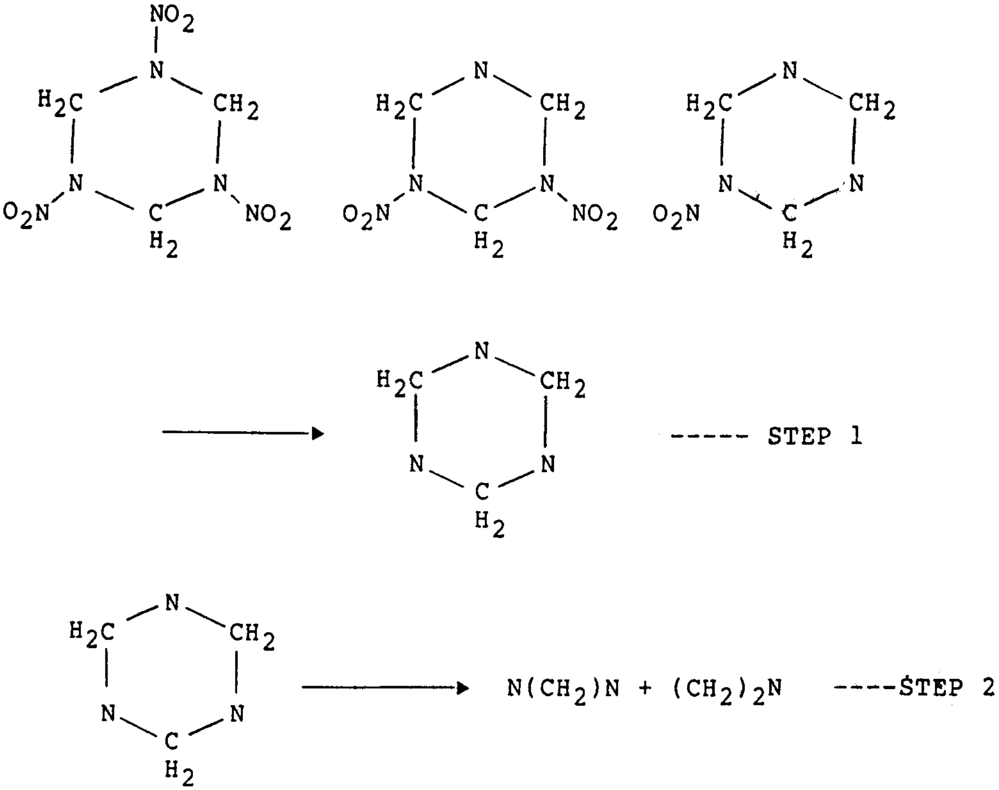

Figure 1(b)

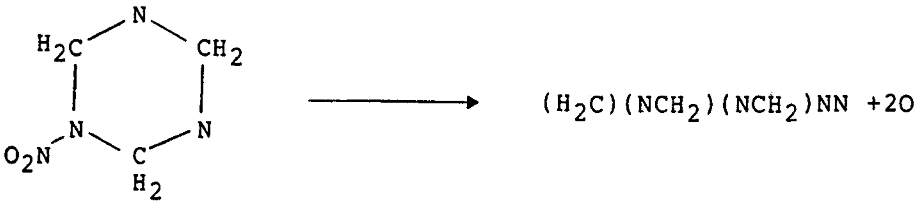

Figure 1(c)