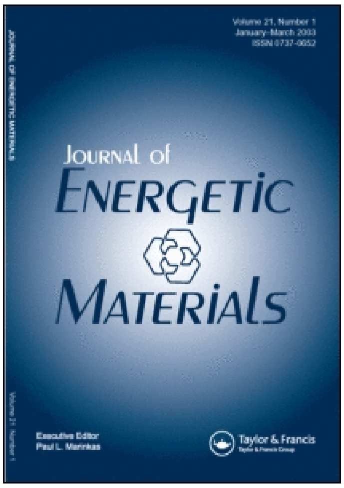

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Real-time analysis of the detonation products of RDX

Normand C. Blais[a]
[a] Chemistry and Laser Sciences Division, Los Alamos National Laboratory, Los Alamos, NM

To cite this Article Blais, Normand C.(1989) 'Real-time analysis of the detonation products of RDX', Journal of Energetic Materials, 7: 3, 207 — 224

To link to this Article: DOI: 10.1080/07370658908014897

URL: http://dx.doi.org/10.1080/07370658908014897

REAL-TIME ANALYSIS OF THE DETONATION PRODUCTS OF RDX

Normand C. Blais
Chemistry and Laser Sciences Division
Los Alamos National Laboratory
Los Alamos NM,87545

ABSTRACT

We have obtained the mass spectrum of the products of detonation from RDX. It was obtained by sampling the freely expanding gases following the detonation of the explosive in vacuum. The time evolution of the products was measured and thereby also the molecular velocities of the species. At the threshold of ion arrival, almost all of the molecules had a common velocity, 8.8 km/s. The spectrum was dominated in intensity by H_2O (ions at M=17,18), followed by important transient species HNCO and NCO. Also we found that the more stable molecules HCN, N_2, and CO had significant intensity. We compare our spectrum with the products found from other studies, such as thermal decomposition, laser ionization mass spectrometry, and the detonation products from detonation under conditions close to equilibrium.

INTRODUCTION

We report here the mass analysis of the products from the detonation of RDX following the subsequent free expansion of these products after detonation. The chemical nomenclature of this compound is hexahydro-1,3,5-trinitro-1,3,5-triazine($C_3H_6N_6O_6$). RDX has been well studied in both the solid and liquid states in an effort to reveal the mechanisms that make it an explosive. Its thermal decomposition, both by rapid and by slow heating has been reported extensively over temperature ranges that include both solid and liquid phases. The thermal motions of the molecule in the solid and the bearing of these motions on condensed phase decomposition has been investigated.[2] The melt phase has been characterized[3] and the decomposition under pressure and high heat rate has been studied.[4] Unimolecular decomposition of RDX using multiple photon excitation in a molecular beam has provided a detailed picture of the important pathways for the thermal decomposition of the isolated molecule.[5] Additional reactive properties of RDX are available from the studies of HMX, which is a very similar explosive and whose properties have been studied even more extensively. Deuterium isotope effects in HMX decomposition have been reported,[6] and the reaction rates of the important decomposition mechanisms have been estimated.[7] All of this work is now leading to serious efforts to elucidate theoretically the details of the molecular processes that lead to energetic decomposition.[8]

Ultimately, it is expected that such studies will lead to an understanding of the chemical processes that provide the energy to propagate a detonation in explosives such as RDX. True detonations in RDX have been studied and the products identified and measured.[9] However, these products are representative of an equilibrium state far removed from the conditions at detonation, and their composition was used to obtain the energy release of the explosive. A relatively simple mass spectrum was obtained consisting of a few stable chemical species whose relative concentrations can be interpreted to indicate the temperatures at which they were formed.

Our experimental conditions are unique in that we can examine detonation products while they are still far from equilibrium conditions. Because of the free expansion of the products into a vacuum, no collisions with ambient gases or with apparatus walls occur before measurements are made. Also, the expansion quickly reduces the number of energetic collisions between the products to a point where the composition of the product constituents no longer change. A model calculation of our experiments suggest that this "freeze-out" point occurs from 1 to 2 µs after the detonation has traversed the explosive charge and the expansion starts. This is the "real-time" relevant to our analysis procedure. This results in a rich mass spectrum compared to steady state measurements, and the species serve to identify the reactions that are important prior to quenching by the expansion. Several measurements of this kind have been reported previously; three of these were studies of commonly used explosives[11-13] and one describes work on a simple chemical that detonates in the condensed phase, nitric oxide.[10]

We will compare the mass spectrum we obtain with steady-state measurements, and with some of the features observed in thermal decomposition work.

EXPERIMENTAL

The apparatus has been described previously.[10,11] Briefly it consists of three parts: a large vacuum vessel in which the explosive charges are detonated, an ultrahigh-vacuum vessel housing a mass spectrometer, two chambers connecting them through small apertures and pumped separately. The detonation products enter the mass spectrometer as a molecular beam formed by the apertures.

Each measurement of ion intensity at a selected mass requires the detonation of an RDX charge. The time evolution of any product species at the quadrupole mass analyzer changes fast enough that the quadrupole cannot be scanned sufficiently rapidly to obtain a meaningful spectrum.

But at any mass setting the data acquisition is fast enough to measure that time evolution. Therefore, only selected masses are investigated where we can reasonably expect to observe products. Moreover, because of the shot-to-shot variation of product generation, this method of product analysis requires that several shots be made for a decent intensity measurement. An advantage does accrue in that the product molecular velocity can be obtained by time-of-flight methods, and we feel that there is information contained in the time evolution of a product about the formation of that product (although we have not been able to capitalize on that feature very much here).

Normally we use our mass spectrometer so that it is a fairly sensitive molecular beam detector. The ionizing electron current is 10 ma with an energy of 100 eV. Under these conditions about 1/1000 product molecules that enter the detector are counted. In addition to the mass spectrum taken under these conditions, we also obtained one with a lower electron energy of 25 eV for comparison. At this lower energy we could obtain a maximum of 4 ma electron current, so that the sensitivity of the apparatus was reduced considerably and only the more prominent masses were included. The reason for this additional spectrum will be discussed later. We also repeated many of the individual mass runs with reduced emission current to ensure that our counting system was not saturated.

The RDX charges were pellets 4 mm diameter by 3 mm high at a density of 1.5 to 1.6 gms/cm^3. They were detonated using electrically driven Kapton slappers 1/40 mm thick and 1.5 mm diameter. The products we obtained were therefore free of contamination from booster charge species. We ascertained that these explosive charges were detonating by applying "witness" plate tests to a few trial assemblies.

RESULTS

Figure 1 is a histogram representing how the data appears on the MCS display. The number of counts appearing in each channel of the scaler is plotted for each channel, except that instead of labelling each channel on the horizontal axis we indicate the time after detonation that each channel accumulates those counts. Each channel receives counts for 10 us. Data from two mass settings are shown,M=18 and M=43. We choose to illustrate these two because they differ in their count rate intensities by a factor of 10 (the detector sensitivity was reduced 1/10 normal for M=18), and also because M=43 is nearly 2.5 times as heavy as M=18. Yet the onsets of the earliest arriving products differ by only 20% and the peak intensities are almost at identical times. This is because the velocities of the products are determined by the free expansion that occurs after detonation instead of by the thermal energies acquired from the heat release of the chemical reactions. If the two products, M=18 and M=43, had velocities characteristic of a common thermal energy, the arrival times would be shifted with respect to each other by times differing by more than 50% over the entire distribution. It is tempting to suggest that the difference in the onset times indicates that the M=43 product is formed slightly later in the product history than the M=18 product. We find some justification for this conjecture from the fact that we observe product onset for intermediate masses such as M=28 to be at times characteristic of M=18 rather than at times intermediate between M=18 and M=43. It is not unlikely that the difference between the two distributions at longer times is because the M=43 signal slightly saturated the counting system. Except for very low intensity masses, these two time distributions are reasonably

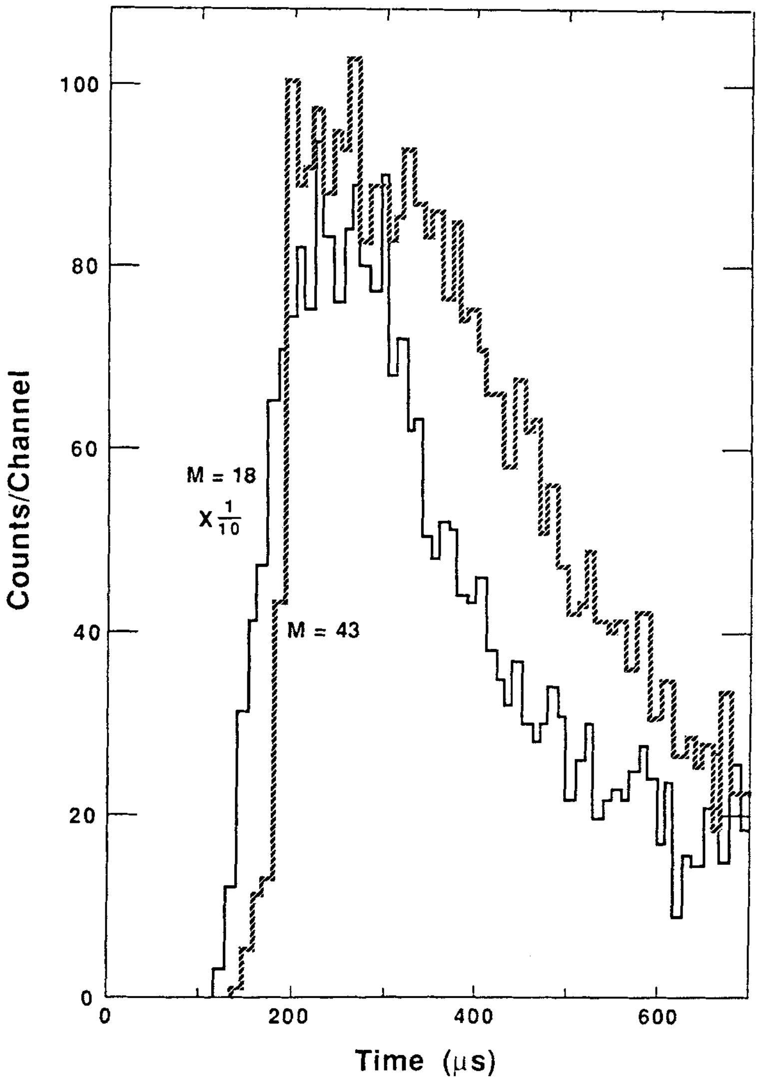

FIGURE 1

Histogram of the data as it appears in the MCS. The vertical axis is the number of counts recorded in each channel of the MCS. The horizontal axis is obtained by noting that 10 μs have elapsed at the end of each channel. Two sets of data are shown, one for M=18 and the other for M=43. The sensitivity of the detector was reduced by 10 for the M=19 data.

representative of the ion signals we obtained for the other selected masses we investigated.

Mass spectra of the detonation products are shown in Fig. 2. The two panels differ in that Fig. 2a was obtained while operating the mass spectrometer with an electron energy of 100 eV and Fig.2b at 25 eV. As we described in the Experimental Section, each mass intensity measurement required a detonation, so that Fig. 2 is not a standard mass spectrometric scan. For each distribution of the kind shown in Fig. 1, we added together all of the counts up to channel 40. These were averaged over the number of trials taken at any mass setting and adjusted for the mass transmission function of the mass filter. At least four to six trials were included at each mass where significant intensity was measured, and six to ten where we found high intensity (such as M=14 to M=18). At least two trials were made for masses where few or no ions were obtained. The circles in Fig. 2 represent masses that we investigated but where no clearly measurable intensities were obtained. We limit our analysis to the first 40 channels because we feel that this group of products is the most likely to be representative of those products formed closely behind the detonation front. It also eliminates the inclusion in the analysis of any products that may have collided with apparatus walls before acquiring the appropriate direction to enter the detector. In constructing these spectra we did not convert the time density distributions to flux because all of them were sufficiently similar that the results would not be different within the statistical errors.

We did not observe any ion signals with significant intensity above M=60, which is why we terminate Fig. 2 at that mass. But we did look at the specific masses 62, 74, 76, 87, and 97.

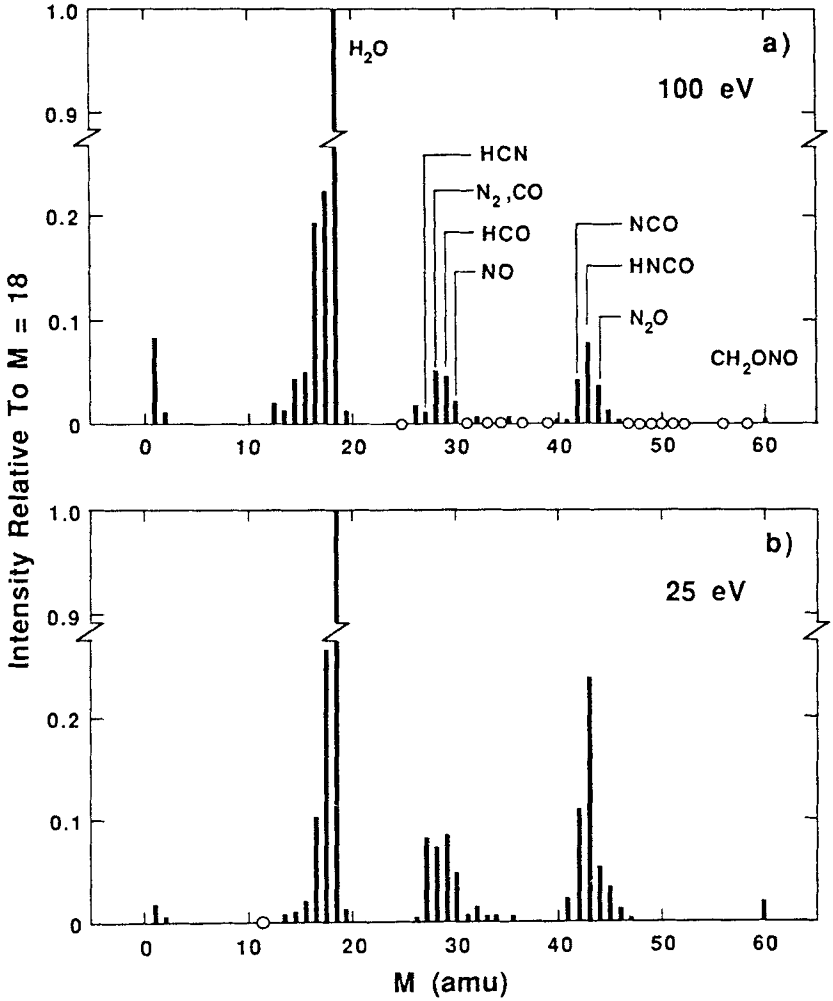

FIGURE 2

The mass spectrum of the detonation products of RDX. The upper panel, part (a) was taken with the mass spectrometer electron energy at 100 eV. The lower panel is part (b) and an electron energy of 25 eV was used. The intensity of each mass was obtained by summing the total number of counts for MCS channels 1 to 40 for data such as shown in Fig. 1.

In these spectra we have not made any adjustments for the product ionization efficiency. To make these adjustments requires knowledge of the identity of the species that produced the ions. In fact, we cannot positively identify the atomic species in the detected ion itself because of the limited resolution of our mass analyzer. Under the conditions for which we took this data, our quadrupole could resolve completely only 1 in 50 amu. Therefore, at M=28, the ions could be a combination of N_2^+, CO^+, NCH_2^+, etc. and at M=42, we could be collecting NCO^+, NCH_2N^+, $CH_2NCH_2^+$, and so forth. What we have chosen to show in Fig. 2 is thus the raw data and a meager interpretation as to the identify of the parent molecules that produce the ions at each mass. Our choice in the interpretation we make is based mostly on the notion that these molecules should be as simple as possible and they should be as stable as possible. Ideally, a reasonably good guess about the ion composition can be made by resorting to the fact that the relative ratio of the atoms in the spectrum must be the same as the explosive. So our product choice is also guided by the necessity to optimize this atom balance.

We are not able to obtain a very satisfactory atom balance with the quantitative features of the spectrum in Fig. 2a, at least to the extent that we succeeded in obtaining with other explosives.[10,13] Using the spectrum at 100 eV and adjusting the ion intensities for the appropriate ionization efficiency for its assigned parent molecule, the imbalance in the atomic ratios is serious. It amounts to a factor of 2 or 3 too much H and O or too little N and C (but the C/N ratio is reasonably good). The most likely source of the problem is the molecular beam detector through the process of electron impact dissociative ionization. One or more species in the product beam do not become ions of the same mass upon electron impact, but dissociate to an ion and a neutral fragment, the latter escaping detection. This process is a familiar one to mass spectrometrists and very often the complexity that it introduces into a spectrum can be overcome once its presence is realized. For stable species the fragmentation patterns are well known and corrections to the spectrum are possible. It is also possible to change the fragmentation pattern of molecules by changing the electron energy and thus discern the identity of the parent neutral if the energy change is sufficient. Many of the molecular species that are found in the detonation products we examine are not stable to the extent that their fragmentation patterns can be measured independently, so we resorted to lowering the electron energy to obtain the spectrum of Fig. 2b.

Comparing both panels of Fig.2, shows that there are definite differences in some parts of the spectrum. Relative to the M=18 intensity, M=1, 12, 14, and 26 are lower by at least a factor of 4 in the low energy spectrum, while M=27, 41, 42, and 43 are increased by the same amount. We interpret these differences as an indication that the masses showing the reduced intensity are fragment ions from dissociative ionization. The first three correspond to H, C, and N atoms, which we probably would have assigned as fragment ions even before doing the lower energy spectrum. We claim that those masses that increased intensity are not fragment ions, but are ions of parent molecules for which fragmentation to smaller ions upon electron impact is a major pathway. So we are assuming that by reducing the electron energy we are affecting the dissociative ionization probability for molecules that fragment much more than we are changing the direct ionization probability relative to M=18. We think that we can justify this assumption. An electron energy of 25 eV is about double the ionization threshold of the molecules we are concerned with here and most of the scaled ionization efficiency curves are similar. The dissociative ionization is strongly affected by lowering the energy because the threshold for the process is higher in energy than ionization by at least the bond energy between the fragments and often much more than that. With a lower electron energy, the branching between fragment ions and parent ions becomes more favorable toward the parent ion pathway. M=18 is certainly H_2O and while it too fragments noticeably it is not serious that we use it as a reference for both spectra, since the ratio of M=17 and M=18 is nearly the same for both energies. We could have used M=28 (which is either N_2 or CO, neither of which fragment significantly) and obtained the same results within our uncertainties.

Using the reduced-energy spectrum of Fig.2b improves the atom balance considerably but the remaining imbalance is still outside our experimental uncertainties. So besides fragmentation of molecules we may also be losing some of the ion fragments from detection because of the kinetic energy associated with ion fragmentation. H^+ is the most likely source of the loss. It is not reasonable to suggest that we can not obtain a good atom balance because there are important contributions from masses higher than M=60 that we have missed. A sufficient presence of products with the necessarily high heats of formation would imply that our explosive samples are not detonating.

DISCUSSION

The molecular assignments that we have shown in Fig.2a are the important parent species in the detonation products of RDX that produce the ions at the masses shown. Ions at other masses are either from molecules of minor importance or else we feel that they are fragments. Mass 18 is certainly H_2O, and there are several reasons for asserting that it is a primary product. It is the most intense signal we measure of any of the detonation products and it is about two orders of magnitude more intense than any of the mass spectrometer background. Its molecular velocity corresponding to the threshold of the ion signal is 8.8 km/s and that of the highest number density is about 5 km/s so that these molecules have a kinetic energy of 2.2 eV. Also, M=17 has the correct intensity to be the OH^+ fragment always observed with H_2O. We think that HCN (M=27) and HNCO (M=43) are probably the next most important constituents because they had large intensity increases when the electron energy was decreased. For the same reason M=42 is a primary product and we assigned it to be NCO, but it may have contributions from other species such as CH_2CO. It was surprising to see the peak at M=60 increase with the lower electron energy, but it is still small and could be CH_2ONO. The remaining products, N_2 and CO (M=28), HCO (M=29), NO (M=30) and N_2O (M=44) are clearly present but they appear to be lower in abundance.

Most of these products are also observed as gaseous products in the thermal decomposition studies of RDX[1,4,14-16]. However only Oyumi mentions HNCO and then as a minor product. A quantitative comparison of our spectrum with the decomposition results is not possible because they often do not include in their report some of the product fractions, such as for H_2O. If we omit considering H_2O, and compare the relative abundances of M=28, 30, and 44 there is reasonable agreement, allowing for the variations between the decomposition results. We agree with Farber in the fraction of M=42 in this limited product sample and also with M=46 he and Oyumi report in their high pressure results. The amount of product we find at M=27 and M=46 is much less than Oyumi reports at atmospheric pressure and high heat rate. Either NO_2 or a parent ion of HCO_2H has a mass peak at M=46, so that we can say that neither nitrogen dioxide nor formic acid is an important detonation product.

It is in the region of product masses greater than 60 that we differ most from the thermal decomposition experiments. Most of the mass spectrometric measurements[15,16] indicate large amounts of product out to M=148. Farber reports significant mass peaks at M=74, 82, 83, 102, 120, 128, 132 , and 148. As we pointed out earlier, we should not expect much product at heavier masses from detonation and we find none except for a small amount of M=60.

Zhao reports an extensive list of products from the infrared unimolecular decomposition of RDX. A few of our major products appear in that list, notably M=27, 30 and 44, which they show as having considerable flux. Here also we find much less NO_2, M=46. Most importantly, they report no H_2O at all, which is our most intense signal. Not too much significance should be placed in contrasting these results, since energizing an isolated molecule to dissociation can be at most only one part of the process of detonating RDX. Their results also indicate a large amount of product at masses of 60 or more, since they find that the dominant primary decomposition path is symmetric triple fission of the RDX.

The decomposition of solid RDX by laser irradiation has been investigated by Tang,[17] who suggests that this method (LIMA) is perhaps more suited for understanding the detonation process. Both positive and negative ion spectra can be examined. Most of the positive ions from RDX are, as in our results, in the mass region less than M=60, although there are observable peaks up to M=130. The most intense ion masses are at

M=28, 30, and 42, which they attribute to N_2 and CO, NO and $N(H_2C)_2$ (which could also be NCO). Some H_2O is present but in lower intensity. In some respects then, their positive ion spectrum is more similar to ours than are the thermal decomposition spectra, although they observe very little HCN or HNCO.

Impact-induced decomposition of RDX has been reported.[18] One of these[18a] lists five gaseous product species, but unfortunately H_2O is not one of them. There data indicate that M=28 (CO and N_2) has about double the composition of M=44 (N_2O and CO_2), while we find more nearly equal amounts. Measured relative to these two masses they also find much larger amounts of M=2 (H_2) than we find. They also report some formaldehyde formation but no quantities are listed. Some of the ions at M=28, 29, and 30 that we see may be from formaldehyde, but the amounts must be small. Another work[18b] only includes analyses of solid residues. More extensive measurements of this kind would be very nice to compare with.

Finally, we compare our product spectrum to the products obtained under conditions much more nearly equilibrium than ours.[9] We combine the N_2 and CO for these results, since they would appear as one ion peak at M=28. Using M=18 as the standard in the same way as for our data the product masses are almost entirely M=28, 18, 44, and 12 in order of diminishing intensity 1.7, 1.0, 0.6, and 0.2 respectively. Very small amounts of H_2, NH_3, CH_4, and HCN are also listed. For the equilibrium results N_2 and CO have the largest intensity followed by H_2O, just the opposite of our results. As we explain earlier, M=28 is not one of the ion peaks that we feel are being lost to detection in our mass spectrometer. There is no reasonable instrumental correction by which we can improve the M=18 to M=28 ratio we find to correspond to the equilibrium results.

We claim that other molecules such HNCO, NCO, and HCN are more abundant. Similarly M=44, which we place as N_2O but which we cannot distinguish from CO_2, is not an important product ion here.

CONCLUSION

The molecular species that we find in the free expansion of the detonation products from RDX are H_2O, HNCO, NCO, HCN, HCO, N_2, and CO and NO in the relative order of intensity. We are uncertain about the ordering of intensity because we don't obtain a good atom balance between initial material and products. Nonetheless, we feel certain that we have not missed any important product in our list by virtue of having investigated the spectrum under widely varying conditions of product detection.

All of the species that we find are also found as gas products in one or another of the various decomposition measurements we have compared with. It is with the comparison of the relative abundances of the products that we differ, indicating that the overall reaction scheme by which they were formed is different. In general, we obtain many more transient molecules such as HNCO and NCO than are found in thermal decomposition experiments or don't appear at all in equilibrium products and also we see highly reactive substances as HCN and HCO. On the other hand we obtain very little NO_2, the production of which is known to be one of the important initial steps in thermal decomposition,and of course none of the solid products or high mass products.

ACKNOWLEDGMENT

We thank James Griffin and Sylvia Trujillo for fabricating the RDX pellets and the slappers. We also want to recognize the efforts of Wilbur Fernandez in the putting the experiments together and keeping the apparatus going.

THIS PAPER WAS PREPARED UNDER THE AUSPICES OF THE U S DEPARTMENT OF ENERGY.

REFERENCES

1) K. P. McCarty, M. W. Beckstead, and R. L. Simmons, "HMX Propellant Combustion Studies" AFRPL-TR-76-59, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, CA 93523 (1976).

2) R. J. Karpowitz and T. B. Brill, J. Phys. Chem. 87, 2109 (1983).

3) R. J. Karpowitz and T. B. Brill, Combust. Flame 56, 317 (1984).

4) Y. Oyumi and T. B. Brill, Combust. Flame 62, 213 (1985).

5) X. Zhao, E. J. Hintsa, and Y. T. Lee, "Infrared Multiphoton Dissociation in a Molecular Beam" ONR NR 659-819/7/87, Office of Naval Research, 800 N. Quincy Street, Arlington, VA 22217, also submitted to J. Chem. Phys.

6) S. A. Shackelford, M. B. Coolidge, B. B. Goshgarian, B. A. Loving, R. N. Rogers, J. L. Janney, and M. H. Ebinger, J. Phys. Chem. 89, 3118 (1985).

7) R. Shaw and F. E. Walker, J. Phys. Chem. 81, 2572 (1977).

8) C. F. Melius and J. S. Binkley, Proceedings, the 21st Symposium (International) on Combustion, Munich FRG, August 3, 1986.

9) D. L. Ornellas, "Calorimetric Determinations of the Heat and Products of Detonation for Explosives: October 1961 to April 1982" UCRL-52821, Lawrence Livermore National Laboratory (1982).

10) N. C. Blais and N. R. Greiner, J. Energetic Mater., submitted.

11) N. C. Blais and J. J. Valentini, Preprints, The Eighth Symposium (International on Detonations, Albuquerque, NM, July 15, 1985, page 425.

12) A. Hoh and F. Aulinger, Dyn. Mass Spectrom. 5,165 (1977).

13) N. C. Blais, J. Energetic Mater. 5, 57 (1987).

14) A. J. B. Robertson, Trans. Faraday Soc. 44, 677 (1948).

15) J. N. Bradley, A. K. Butler, W. D. Capey, J. R. Gilbert, J. Chem. Soc. Faraday II 73, 1789 (1977).

16) M. Farber and R. D. Srivastava, Chem. Phys. Lett. 64, 307 (1979).

17) T. B. Tang, M. M. Chaudri, and C. S. Rees, J. of Materials Science 22, 1037 (1987).

18) (a) A. J. B. Robertson and A. D. Yoffe, Nature, Lond. 161, 806 (1948).
(b) J. Sharma, J. C. Hoffsommer, D. J. Glover, C. S. Coffey, W. Forbes, T. P. Liddiard, W. J. Elban, and F. Santiago, Preprints, the Eighth Symposium (International) on Detonation, Albuquerque, NM, July 15, 1985, page 931.