Initial Thermochemical Decomposition Mechanisms of Energetic Ingredients

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The deuterium isotope effect was used to investigate the rate limiting reactions in the decomposition of nitramine propellant ingredients. HMX and RDX and their deuterated analogs were synthesized. These ingredients were decomposed in an isothermal scanning calorimeter that measured the rate of decomposition. Similar experiments were performed in test tubes that were quenched in liquid nitrogen to determine extent of reaction versus time. The magnitude of the observed deuterium isotope effects suggests that the overall rate of decomposition is controlled by the C-H bonds in these ingredients.
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Introduction

This project addresses fundamental research barriers in understanding thermochemical decomposition processes which directly affect propellant ingredient requirements and future chemical propulsion concepts. A significant advancement will result in the elucidation and potential control of these processes as they apply to propellant hazards, storage, precombustion, and overall performance characteristics. Ultimately, this project could provide advanced knowledge to achieve vastly enhanced mechanical, physical, ingredient compatibility properties with longer storage and decreased life cycle costs, more stable and less hazardous high energy propellant formulation, decreased ignition delays, and improved combustion tailoring.

Thermochemical decomposition processes are recognized chemical reaction precursors to propellant combustion. While these precombustion decomposition processes are known to proceed through sequenced radical reaction mechanisms, their detailed steps are not fully understood. The primary and rate-determining steps, which occur early in the overall reaction mechanism but not necessarily first, control precombustion events and probably contribute to long term propellant ingredient instability and aging problems as well. Past thermochemical decomposition studies investigated the overall reaction mechanism at ambient pressure over a given temperature range. Only recently has the importance of the early or initial portion of the reaction mechanism and its detailed steps at various pressures become generally recognized. For example, a new approach used to investigate TNT verified the critical reaction steps occurred during the initial stage of thermochemical decomposition; this controlling portion had been ignored in earlier studies. A later investigation that employed this new approach with TATB afforded similar results. These findings subsequently generated another study of TNT which revealed that the thermochemical decomposition mechanism may depend upon phase state (gas, liquid, solid) and can be drastically altered by small amounts of catalytic additives. Additionally, no systematic thermochemical decomposition investigations have been reported which determine possible pressure effects upon the detailed steps in the reaction mechanism, but, such effects are suspected.

Recent advances in instrumental diagnostics, mechanistic elucidation techniques, and novel combinations thereof now show promise for detailed identification of the primary and rate-determining steps in thermochemical decomposition and for determination of their kinetic parameters.
Systematic correlations between an ingredient's molecular structure and its elucidated thermochemical decomposition reaction mechanism have been attempted. A correlation between molecular structure with an ingredient's initial and rate-limiting reaction steps will prove especially important since these two interdependent molecular features determine the unique properties exhibited by an ingredient under a given thermochemical condition.

Program Objectives

The detailed reaction steps in the thermochemical decomposition mechanism of propellant ingredients and the kinetic parameters which drive them have been investigated. Special attention has been given to the primary controlling steps that occur early in the decomposition process. As specific ingredient mechanisms were elucidated, attempts were made to correlate primary thermochemical reaction steps to molecular structure and to establish a systematic relationship between molecular structure and ingredient stability/instability/compatibility properties.

Background

This project focused on exploring in-situ the rate controlling steps of the nitramine oxidizers RDX and HMX. Thermal decomposition measurements were made to ascertain the kinetic parameters by employing isothermal differential scanning calorimetry measurements during the decomposition processes. These decomposition mechanisms are very complicated processes with mechanisms changing with temperature and phase. The solid state decomposition presents further complications to the elucidation process because crystal effects of melting, heat transport, etc., in addition there are competing reactions and subsequent reactions that occur during the decomposition process. The number of decomposition mechanisms suggested in the literature and the number of nitramine studies point out the difficulty of a mechanistic study.

This project chose to employ the kinetic deuterium isotope effect as a means of elucidating in-situ the mechanistic behavior of the reaction sequence. The kinetic isotope effect has long been used as a tool in exploring the mechanism of organic chemical reactions and has been thoroughly studied and documented in such cases. The isotope effect arises due to a change in the kinetic rate of a reaction when an isotopic substitution within a molecule is made. Most commonly a
deuterium is substituted for a hydrogen, which is the case in this project, but the principles hold true for heavier atoms. The deuterium kinetic isotope effect is simply the ratio of the protonated material reaction rate to the reaction rate of the deuterated material. The deuterium isotope effect arises because of the mass difference of the two atoms. This mass difference is assumed not to affect the electronic structure of the molecule and thus the binding forces within the molecule remain the same upon substitution and the potential energy surface of the reaction does not change. The mass of the atoms does affect the vibrational frequencies of a molecule, however. In particular, the ground state energy (or zero point energy) of a molecule is lowered by the larger mass of the deuterium. Thus, more energy is required to completely dissociate the C-D bond than the C-H bond. This energy difference is reflected then in the relative rates of the processes.

In reaction steps where bonds are broken the isotope effect is the largest and is termed a primary isotope effect. If the only contribution to the observed ratio is the difference in the zero point energies, the energy difference between the deuterium and hydrogen substituted bonds required for bond breaking could be obtained from the difference in the stretching frequencies. At room temperature this would produce an isotope effect of 6.4 \((k_H/k_D)\). Since the vibrational frequencies are inversely proportional to the square root of the mass, high temperature deuterium isotope effects should approach the theoretical limit of 1.4. This is an incomplete model, however, as there are many more factors that influence the magnitude of the isotope effect. The symmetry of the transition state, all vibrational modes available to the molecule, and the aptness of the assumptions made concerning the electronic states all could influence the observed isotope effect. An additional complication in using the isotope effect in this project is that the reactions of interest were occurring in the condensed state. Further factors such as crystal lattice breakup, heat transfer, and intermolecular interactions might also influence the observed isotope effect.

If a bond containing the substitution is not broken during the rate controlling step of the reaction, a second type of isotope effect may be observed which is termed a secondary isotope effect. These effects are usually much smaller than the primary isotope effects and arise from the influence the isotopic substitution has on neighboring vibrations and consequently the zero point energy. Secondary effects are commonly observed when the carbon changes hybridization from \(sp^2\) to \(sp^3\) and thus are often used to distinguish between a \(SN1\) and \(SN2\) mechanism. If the isotopic substitution causes a isotope effect of less than one, then this type of secondary effect is termed an
inverse isotope effect. This effect arises largely for the same reasons as the secondary effect, influence of neighboring vibrations and is often observed in reactions where the carbon changes from $sp^2$ to $sp^3$.

The main advantage the use isotope effects provide for the investigation of energetic materials is that the mechanisms can be probed during the actual energetic event. Most reactions of energetic materials are very rapid, normally occurring with several parallel reactions of the secondary products. This makes the elucidation of the rate controlling steps difficult to determine. The isotope effect only shows up if the substituted sites are involved in the rate determining steps and give some indication as to the nature of that step. For these reasons, the deuterium isotope effect has been increasingly used as a probe of energetic materials. A recent thesis concerning the deuterium isotope effects in the combustion of nitramine materials provides a very good discussion of the deuterium isotope effects as applied to energetic materials.

Following are abstracts from two papers that were published under this project and a third paper that will be submitted to the Journal of Physical Chemistry.
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Deuterium Isotope Effects in Condensed-Phase Thermochemical Decomposition Reactions of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

S.A. Shackelford, M.B. Coolidge, B.B. Goshgarian, B.A. Loving, R.N. Rogers, J.L. Janney, and M.H. Ebinger,


Abstract

The deuterium isotope effect (DIE) was applied to condensed-phase thermochemical reactions of HMX and HMX-d8 by using isothermal techniques. Dissimilar deuterium isotope effects revealed a mechanistic dependence of HMX upon different physical states which may singularly predominate in a specific type of thermal event. Solid-state HMX thermochemical decomposition produces a primary DIE, indicating that covalent C-H bond rupture is the rate-controlling step in this phase. An apparent inverse DIE is displayed in the mixed melt phase and can be attributed to C-H bond contraction during a weakening of molecular lattice forces as the solid HMX liquefies. The liquid-state decomposition rate appears to be controlled by ring C-N bond cleavage as evidenced by a secondary DIE and higher molecular weight products. These results reveal the dependence of the HMX decomposition process on physical state and lead to a broader mechanistic interpretation which explains the seemingly contradictory data found in current literature reviews.
Deuterium Isotope Effects in HMX Thermochemical Mechanisms: Decomposition, Deflagration, and Combustion


Minutes of the 20th JANNAF Combustion Meeting

Abstract

The deuterium isotope effect was applied to HMX and its deuterated analog HMX-d8 to investigate the key chemical reactions and molecular bond ruptures which control the global energy release rate in three types of thermochemical events: decomposition, deflagration, and combustion. Although thermochemical processes are quite complex and involve a myriad of stepwise and simultaneous reactions, deuterium isotopes can directly reveal rate controlling chemical reactions and molecular bond ruptures in real time during the energy releasing event itself. Thermochemical decomposition investigations were conducted with solid HMX several degrees below its melting point. The HMX samples proceeded through three physical states: solid, mixed melt, and liquid. We found three distinct deuterium isotope effects; each was different in magnitude and type, and each was dependent upon one of the three HMX physical states. This suggests a change in mechanism and rate-controlling reaction for each condensed phase cited. Investigations in both rapid pyroprobe deflagration and explosive deflagration revealed a single deuterium isotope effect for each, but each isotope effect was different and infers that the rate-controlling reactions depend upon the predominate HMX physical state present during a specific type of thermochemical event. Pressurized glass tube combustion of HMX pellets revealed a primary deuterium isotope effect at pressures of 500 and 1000 psig. This primary deuterium isotope effect confirms in-situ that C-H bond rupture in solid state decomposition ultimately controls the burn rate of HMX during the combustion process.
Deuterium Isotope Effects in RDX Decomposition and Combustion
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Abstract

The kinetic deuterium isotope effect was used to investigate in situ the rate limiting reaction controlling RDX thermal decomposition and combustion. The rates of RDX and deuterium labeled RDX-d6 thermal decomposition were measured using isothermal differential scanning calorimetry, and to RDX/RDX-d6 pressed pellet window bomb combustion studies. In both cases a primary deuterium isotope effect was observed. These results are discussed and compared to isotope effects observed in decomposition and combustion with HMX.

Introduction

Isotope effects have been used by the chemical community for many years, and have been applied to the investigation of both combustion and decomposition. The isotope effect provides an unique method to examine the mechanisms of very fast processes during the actual event. Since the isotope effect is only seen when the rate

determining or slow step of the mechanism involves the isotopically
labeled substituent it provides a good indication of what part
of the molecule is controlling the rate of the overall decomposition
or combustion process.

The deuterium isotope effect is increasingly being used in the
investigation of energetic materials because it provides a way to
sort out the overall rate determining step from amongst the many
parallel chemical and physical processes occurring during a
decomposition or combustion event. Such information can be important,
for example, in determining how to alter a propellant's burn rate or
in understanding the detonation of an explosive. The deuterium
isotope effect has been observed in the investigation of thermal
decomposition and shock initiation of TNT; and in thermal degradation
and initiation of solid TATB. In all these cases the deuterium
isotope effect afforded a convenient method to examine "in situ" the
mechanism of the thermal processes involved. The investigation
of HMX thermal decomposition and combustion processes using the
deuterium isotope effect has been reported. This report concerns
the continuation of that work with RDX.

(1977), "42", 4201; b.) R.N. Rogers, J.L. Janney, M.H. Ebinger;
Journal of Energetic Materials (1983), 133-140
4. S.A. Shackelford, M.B. Coolidger, B.B. Goshagarian, B.A. Loving,
3118-3126
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Flanigan; Propellants, Explos. Pyrotech., in press
Isotope Effects

The kinetic isotope effect arises from a change in the rate of reaction when an isotopic substitution in the molecule of interest is made\(^6\). This substitution is assumed not to considerably change the pathway or the transition state of the reaction mechanism. The rate change is due to the difference in the zero point energy (the ground-state vibrational energy) which depends on the mass of the atoms and is lower when the reduced mass is higher. Therefore the activation energy for carbon-deuterium bond rupture is larger than for carbon-hydrogen by an amount equal to the zero-point energy difference. The differing activation energies result in a larger rate constant for C-H bond rupture as compared to C-D bond rupture. This sort of isotope effect, involving bond rupture, is termed a primary isotope effect.

The primary isotope effect is the one most commonly observed and reported, but deuterium substitution can cause the rate of reaction to increase, which is termed an 'inverse isotope effect'. A third type of isotope effect is the secondary isotope effect which does not involve carbon-hydrogen bond breaking. These are generally thought to involve differences in bending vibrations for H or D in the transition states.

The magnitude of the ratio of rates \(k_H/k_D\) is indicative as to

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which type of isotope effect is being observed, and consequently provides an insight to the rate determining step of the mechanism. A primary isotope effect is generally thought to be above 1.35 at the high temperature limit. A secondary deuterium isotope effect is expected to be between 1.00 and 1.35 and an inverse effect less than one. It should be emphasized that the deuterium isotope effect will only show up in the rate determining step, and only if its transition state involves the substituted site.

**Experimental**

**Synthesis** RDX and RDX-\(d_6\) were prepared in an identical manner starting with paraformaldehyde or paraformaldehyde-\(d_2\) to ensure that any differences observed were related to the deuterium substitution and not to impurities or sample history. The synthesis employed produced a product that was HMX free and completely nitrated. NMR analysis showed the RDX-\(d_6\) to be 98% deuterated.

**Synthesis of RDX (1,3,5-trinitrohexahydro-s-triazine)**

To 28.4 g of phosphorous pentoxide (weighed out under nitrogen) in a three neck 500 ml round bottom fitted with reflux condenser and thermometer, was added dropwise 83.7 g anhydrous nitric acid from an addition funnel. The mixture was magnetically stirred

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and the temperature monitored. The addition of the nitric acid caused an exotherm to 41°C. When the reaction mixture had cooled to 35°C, 2.8 g (0.013 mol) of TRAT (1,3,5-triacetyl-1,3,5-hexahydrotriazine) was added all at once through a funnel. The round bottom was then placed in an oil bath and the reaction mixture was heated at 65°C for 15 minutes. At the end of this time the solution was allowed to cool to room temperature and then poured on ice. The solution was left to stand and the precipitate was filtered and washed with water to leave a clean, white product.

yield: 2.3 g (0.010 mol) (77%) mp. 203°C
1H NMR (DMSO-d$_6$) 6.1 ppm (CON$_2$)

Synthesis of TRAT (1,3,5-triacetyl-1,3,5-hexahydrotriazine)$^9$

Hexamethylenetetramine$^10$, 8.3 g (0.059 mol) was added at room temperature to 33.2 g (0.361 mol) acetic anhydride and magnetically stirred. The solution was then heated at 98°C for 2 hours. The reaction mixture was cooled to 5°C, 20 ml of water was added, and then stirred for an additional 30 minutes. It was then reduced to a viscous yellow liquid by vacuum distillation. Water (20 ml) was added, and the mixture cooled to induce precipitation. The solid

product was filtered and dried over NaOH pellets under vacuum.

yield: 8.65 g (0.061 mol) 70% mp. 96°C
1H NMR (DMSO-d$_6$): 2.1, 5.2 ppm (-CH$_2$-)

RDX-d$_6$, TRAT-d$_6$

All deuterated materials were synthesized in an identical manner as the non-deuterated analogues, substituting the deuterated precursor (i.e. RDX-d$_6$ was made from TRAT-d$_6$).

Thermal Measurements

Isothermal Differential Scanning Calorimetry experiments were performed on a Perkin-Elmer DSC 1B or on a Perkin-Elmer DSC System 4. The samples were weighed into an aluminum DSC pan, which had a 0.1 mm hole drilled into the lid, and were then hermetically sealed. Sample size was 2.00 +/- 0.04 mg. Data was taken from the DSC with a digital recorder and to a Vax 785 for processing. All the runs were done at atmospheric pressure with a slow nitrogen purge.

Combustion Measurements

The combustion experiments were done in a window bomb at 500 and 1000 psi. The RDX and RDX-d$_6$ samples were pressed into cylindrical pellets weighing approximately 900 mg and a density approaching theoretical maximum density. The burn rate measurements were made by observing the combustion process with high speed photography and then calculating burn rates from the film. The pellets were ignited by a
hot wire stretched across the top of the pellet and a slow stream of nitrogen was used to carry combustion products away and provide a clear optic window. The pellets were coated with an inhibitor to assure a horizontal burn pattern. The RDX and RDX-\(d_6\) samples were treated in the same way and the burn rates compared (rate hydrogenated /rate deuterated) to obtain the observed isotope effect.

**RDX Decomposition Results**

The IDSC results are shown in Table 1. A typical IDSC curve is shown in Figure 2 and seems to agree quite well with what has been reported in the literature.\(^{11}\) The thermal decomposition of RDX, at the temperature ranges examined, obeys first order kinetics and shows a primary deuterium isotope effect. This isotope effect would suggest that the rate limiting step in the decomposition of RDX is carbon-hydrogen bond rupture. Under the experimental conditions employed, the thermal decomposition occurs solely in the liquid phase with RDX. By the time the DSC has equilibrated, the decomposition phase has already started and the DSC trace is seen as a slow decay. No induction phase can be seen with RDX. HMX, in contrast, shows a well defined reaching the liquid phase. However, the DSC temperatures were well above the melting point of RDX rather than below it, as with HMX. In


induction phase which could be used to calculate an isotope effect (2). HMX also passed through both a solid and mixed melt phase before view of these differences, therefore, it becomes difficult to make any
direct comparisons to HMX, except perhaps with the liquid decay phase. Future plans include examining HMX above its melting point in order to compare the results directly with RDX. Also other methods will be used to examine RDX below its melting point to more directly compare the results with HMX. These studies will provide an insight as to how temperature affects the isotope effect and the decomposition mechanism.

It is interesting to note that the decomposition of the liquid state of HMX exhibits a secondary isotope effect while that of the RDX liquid state decomposition shows a primary effect. This would suggest that carbon hydrogen bond rupture is the rate controlling step in RDX as opposed to the carbon - nitrogen bond rupture in HMX. It is difficult to explain why the decomposition mechanisms should differ in such similar molecules. It should also be noted that the decay phase of HMX fits a first order kinetic plot as well as the autocatalytic plot. RDX shows first order kinetics but does not fit an autocatalytic plot under our experimental conditions.

**RDX Combustion Results**

The combustion burn rate results are shown in Table 2. If the assumption is made that the burn rate data is directly proportional to the kinetic rate constants and that all the other factors influencing burn rate remains the same for both the deuterated and hydrogenated materials then an isotope effect can be derived from a ratio of the RDX burn rate to RDX-$d_6$ burn rate. The isotope effects thus obtained
are 1.46 at 1000 psi and 1.37 at 500 psi. At the high temperature limit an isotope effect of 1.35 or greater can be considered to be a primary effect (2). So it may be seen that the isotope effect observed in the RDX combustion is a primary isotope effect which would mean that the overall rate controlling step of RDX combustion involves the rupture of the carbon-hydrogen bond. It is difficult to say from these results if the rate limiting steps observed for combustion and slow decomposition are the same. It is conceivable that the combustion process does occur from the liquid phase similar to that occurring in the slow decomposition, indeed both events show the primary isotope effect. However, it is also possible that the combustion processes occur directly from the solid state and that the observed isotope effect is due to solid state decomposition similar to that observed in HMX. Under the conditions that the DSC studies were done no solid state reactions could be observed. In any case, the experiments do show that deuterium substitution does effect the burn rate of RDX with the implication being that the rupture of the carbon-hydrogen bond is the slow step in the combustion process and that the slow step occurs in the condensed phase, not the gas phase. This result is important in that it implies that to significantly alter the overall burning rate of RDX the C-H bond must be altered or the bond rupture catalyzed.

Review of HMX Results

The slow thermal decomposition of HMX was examined by Isothermal Differential Scanning Calorimetry (IDSC) with the resulting scan fitted to an autocatalytic rate law.12 The rate constants and
induction times for HMX and HMX-d$_8$ were then compared to obtain the observed deuterium isotope effect. The results show that three different isotope effects are seen during the course of the decomposition. The initial solid state induction period shows a primary isotope effect, which infers that carbon-hydrogen bond rupture is occurring faster than carbon-deuterium bond rupture. It could be speculated that the initial decomposition involves a nucleation event consisting of the loss of a NO$_2$ radical, which is trapped in the crystal lattice, and then further reacts with an HMX molecule to remove hydrogen. This hydrogen abstraction is thought to be responsible for the observed isotope effect.

The second phase of the decomposition involves a very rapid acceleratory phase as observed by IDSC. This mixed melt stage is a transitory period during which the solid melts to the liquid. An inverse isotope effect is observed during this phase of the decomposition, which means that the decomposition processes are faster with deuterated HMX than with hydrogenated HMX. This implies that the mechanism of the decomposition has shifted so that the slow step of the decomposition is other than that which produced the initial primary effect. One explanation might be that the most endothermic process occurring during this phase transition involves the melt of the solid. The inverse effect could be explained by noting that the hydrogen bonding in the crystal lattice is weaker with deuterium than

with hydrogen. Consequently, the rate of melting is faster with the deuterated sample, producing the inverse isotope effect.

The third phase of the HMX decomposition, the decay phase, occurs in the liquid state and exhibits a secondary isotope effect, which is indicative of the carbon - nitrogen bond rupture being the slow step of the mechanism.

The combustion experiments with HMX were conducted in a window bomb using cylindrically pressed pellets (96-97% theoretical density) at pressures of 500 psi and 1000 psi. Burn rates were determined with both HMX and HMX-d$_8$ by employing high speed photography to record combustion processes and the burn rates calculated from the films. The ratio of HMX/HMX-d$_8$ was then used as the isotope effect. A primary isotope effect was obtained from combustion experiments indicating that the overall rate controlling process of combustion is the rupture of the carbon - hydrogen bond. If the results of the thermal decomposition can be extrapolated to the combustion event then it would appear that the rate controlling process of combustion is occurring in the solid state, for this is where the primary effect was observed during decomposition.

In a continuation of these studies we wish to report our progress with the investigation of the deuterium isotope effect in the thermal decomposition and combustion of RDX (Figure 1). RDX is structurally similar to HMX but shows remarkably different characteristics. These results will be compared and contrasted to HMX in an attempt to
provide a more complete picture of the key chemical reaction steps and associated bond ruptures which control the overall energy release processes and burn rates of cyclic nitramines.

Test Tube Experiments

In order to gain additional insight into the decomposition process, another experiment was conducted to explore RDX decomposition kinetics. This experiment involved measuring the decomposition of RDX by monitoring its absorption at 236 nm as a function of time. The absorption values at different times yields a direct measurement of the decomposition of RDX, which is different than the secondary observations obtained using IDSC. A comparison of the decomposition rates between deuterated and protiated RDX demonstrates whether an isotope effect is present.

Experimental

A known amount of RDX (RDX-d6), nominally 1.2 mg, was placed into several micro test tubes (Pyrex laboratory glassware, Cat. No. 9820, 6 x 50 mm). These test tubes were placed through holes in a piece of cardboard and the tubes immersed in a silicon oil bath maintained at 212 +/- 1°C. The time of submergence was monitored and a test tube removed every 60 seconds. The tube was cooled first in ice water and then liquid nitrogen to quench the decomposition. After all the test tubes were removed and quenched, the RDX (RDX-d6) was dissolved in acetonitrile and solutions made to a volume of 10 ml. An
acetonitrile blank was run on the UV spectrometer to determine where acetonitrile absorbs. An RDX (RDX-d₆) blank was then run to determine the undecomposed absorbance. The test tube solutions were run to measure their absorbances. The extinction coefficient E was obtained from the RDX (RDX-d₆) blank (cell width = 0.1 cm). E was found to be 11,264 l cm⁻¹ mol⁻¹ for RDX and 10,880 l cm⁻¹ mol⁻¹ for RDX-d₆.

Results and Discussion

Using these values for E, the amount of undecomposed RDX (RDX-d₆) was determined. The first order plots of absorbance vs. time for each compound is shown in Figures 1 and 2. The slopes of the lines correspond to the decomposition rate. The ratio of these two slopes shows an isotope effect of 1.72, which is taken to be a primary effect. This direct measurement of the decomposition further supports that C-H bond cleavage is the rate-limiting mechanism in RDX decomposition.

Conclusions

The deuterium isotope effect has been used to examine both the slow decomposition and fast combustion processes of RDX. In both cases it has been seen that a primary deuterium isotope effect has been observed indicating that carbon-hydrogen bond rupture is the overall rate controlling step in each process. It is significant that an isotope effect has been seen in the combustion of RDX because it further validates the use of isotope effects as a tool in the elucidation-
tion of combustion mechanisms. It shows that the effect is not limited to a single isolated case, such as HMX, but is a more general phenomenon. Thus it further validates the results obtained previously with HMX. The different results obtained with RDX as compared with HMX also serves to further point out the difference in behavior between two such very similar nitramines.

The slow thermal decomposition and combustion mechanisms are very complex processes, involving many different chemical and physical reactions. The isotope effect has helped to sort out the slowest of these reactions and has proved to be a valuable aid in investigating these mechanisms "in situ". They have helped to show that a burn rate change may be achieved by altering the condensed material and specifically the carbon-hydrogen bonds of RDX and HMX.

**TABLE 1**

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<tr>
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<tr>
<td>515</td>
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(Error is at 95% confidence level with n=12 at 510K. Data at 505K is reported as preliminary data.)
<table>
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<tr>
<th></th>
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<td>217+/-13</td>
<td>567+/-72</td>
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| 1000 psi |    |       |    |       |
| RDX 254 | 208 | 540   | 399|       |
| RDX 293 | 229 | 685   | 406|       |
| RDX 302 | 235 | 600   | 423|       |
| RDX 337 | 209 | 501   | 357|       |
| RDX 322 | 213 | 508   | 349|       |
| 297+/-31| 217+/-13| 567+/-72| 387+/-34|

(Values reported are in/sec. Reported error is 95% confidence level.)
Figure A-1. First order plot of RDX decomposition.
Figure A-2. First order plot of RDX-d6 decomposition.