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IN-SITU DETERMINATION OF EXOTHERMIC TRANSIENT PHENOMENA : ISOTOPIC LABELLING STUDIES

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Résumé

Les effets isotopiques de la deutération sur la cinétique en phase condensée (DIE) et l'étude des produits obtenus par échange isotopique (IPE) représentent deux approches complémentaires, non perturbantes in-situ pour la détermination des mécanismes transitoires qui règlent les processus de libération exothermique d'énergie des composés énergétiques et des explosifs usuels. L'application des DIE et IPE aux cas complexes fortement exothermiques liés à la décomposition, la combustion, l'explosion thermique, et la détonation révèle sélectivement la clé des mécanismes transitoires microscopiques et permet, parfois, de suggérer un mécanisme commun à ces différents événements. Les recherches par DIE peuvent identifier l'étape de la réaction chimique qui règle véritablement la cinétique et la rupture de la liaison covalente associée responsable du contrôle de la vitesse de libération de l'énergie globale d'un cas donné exothermique. L'approche DIE suggère aussi que le facteur qui contrôle la vitesse peut changer avec l'état physique d'un composé énergétique, lequel en retour est déterminé par le type d'expérience et les conditions aux limites externes. La technique IPE ajoute un plus aux résultats DIE en montrant dans quelle mesure toutes les liaisons covalentes sont rompues et désigne l'itinéraire selon lequel des réactions chimiques transforment des espèces transitoires en produits lors d'une séquence globalement exothermique d'événements. De plus, IPE peut délimiter avec précision dans quelle mesure les interactions des espèces transitoires réactives sont limitées par la diffusion dans un composé pur ou dans un mélange de composés au cours d'une détonation. L'information unique sur un mécanisme microscopique obtenue à partir des deux approches DIE et IPE apporte aussi un maillon scientifique entre les comportements caractéristiques microscopique et macroscopique rencontrés au cours d'événements exothermiques de composés énergétiques. On discute ici les approches en phase condensée DIE et IPE, et les cas où ils relient des résultats micro- et macroscopiques sont soulignés.

Abstract

Condensed phase kinetic deuterium isotope effects (DIE) and isotopic product exchange (IPE) represent two complementary, non-intrusive in-situ approaches for determining the transient mechanistic features which regulate the exothermic energy-releasing processes of energetic compounds and conventional explosives. Application of DIE and IPE to the complex highly exothermic events represented by decomposition, combustion, thermal explosion, and detonation selectively reveal the key microscopic transient mechanistic features and in some cases, may suggest a mechanistic commonality among these various events. DIE research investigations can identify the actual kinetic rate-limiting chemical reaction step and

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associated covalent bond rupture responsible for controlling the global energy release rate of a given exothermic event. The DIE approach also suggests the rate-controlling feature can change with the physical state of an energetic compound, which in turn is determined by an experiment's design and externally applied boundary conditions. The IPE technique supplements DIE findings by showing the extent to which all covalent bonds are ruptured and infer the route of the chemical reactions by which transient species reform into products during an event's overall exothermic process. Additionally, IPE can quantify the extent to which reactive transient species interactions are limited by diffusion in a pure compound or in a mixture of compounds during a detonation event. The unique microscopic mechanistic information obtained from both the DIE and IPE approaches also provides a scientific link between the microscopic and macroscopic behavioral characteristics encountered in the exothermic events of energetic compounds. The condensed phase DIE and IPE approaches are discussed, and cases where they bridge micro-and macroscopic issues are noted.

INTRODUCTION

Mechanistic investigation of the autocatalytic, exothermic processes produced by the decomposition, combustion, thermal explosion or detonation events of energetic compounds and conventional explosives presents a difficult research challenge. Even the slowest of these exothermic events, thermochemical decomposition, produces a myriad of sequential and simultaneous condensed phase chemical reactions, plus physicochemical changes, during its short-lived and environmentally hostile energy-releasing process. Use of the condensed phase deuterium isotope effect (DIE) and isotopic product exchange (IPE) approaches permit the selective identification, measurement, and evaluation of key microscopic, transient, mechanistic features which control the energy-releasing processes associated with these various energetic events. In doing so, they further provide information capable of bridging the scientific understanding between the fundamental microscopic phenomena and more visible macroscopic behavior or properties associated with high energy material exothermic events.

Condensed Phase Deuterium Isotope Effects (DIE). The deuterium isotope effect has been used extensively in mechanistic studies of well-defined gas phase and solvolyzed chemical reaction systems. Within the last several years, the DIE also has proved its mechanistic value for selectively determining the key kinetic chemical reaction steps and thermal physicochemical characteristics which control the overall exothermic processes involved with an energetic material's slow decomposition, rapid degradation, combustion, thermal explosion, and detonation.[1-11] The DIE selectively identifies this slowest chemical reaction and its associated covalent bond rupture amid a myriad of other more rapid reactions during the exothermic process itself. In processes which are kinetically controlled, the slowest chemical reaction step is the key rate-limiting mechanistic feature. While not necessarily a compound's first covalent bond rupture, this slowest mechanistic bond rupture step must occur sometime during the energy releasing process, and in doing so, determines the overall rate of the high energy event. The DIE is detected by a change in the chemical reaction rate when a deuterium nuclei is substituted for a normal hydrogen atom at a specific location in a compound's molecular chemical structure. This rate change is caused by a difference in ground state vibrational energy between the carbon-hydrogen (C-H) and identical, but stronger carbon-deuterium (C-D) bond (Figure 1). When the slowest reaction step involves direct rupture of the C-H/C-D bond or rupture of a chemical bond in its immediate vicinity, a DIE

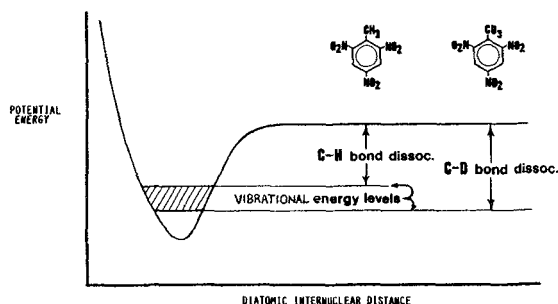


Figure 1

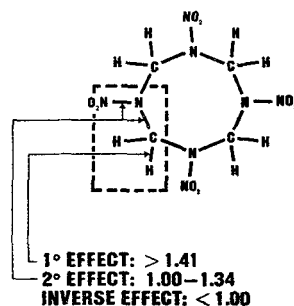


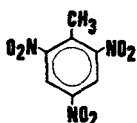
Figure 2

results. Three types of DIEs are possible as shown by the HMX molecule in Figure 2. Rupture of the C-H bond during the slowest chemical reaction step provides a primary (1°) DIE where the hydrogen/deuterium rate constant ratio (k_h/k_d) is theoretically above 1.41 at its high temperature limit.[12] Experimentally, however, a 1.35 value can be acceptable as a valid lower limit for a 1° DIE.[13] Cleavage of a bond either adjacent to the deuterium labeled C-H bond or one bond further away would normally provide a value in the 1.34 to 1.00 range, although a 2° DIE value increases somewhat when more than one deuterium atom is substituted at the same site. Because of the very high temperatures found in the exothermic events discussed, a 1° DIE would tend to approach its minimum high temperature value, and a 2° DIE which would be similarly affected, would not be expected to be found near its upper value limit (2). Finally, there can be an inverse DIE where $k_h/k_d < 1.00$ which results from an increase in the C-H/C-D bond's force constant.[14]

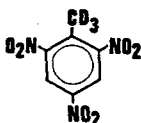
The first mechanistic application of the condensed phase DIE approach with an energetic explosive compound was reported for the slow decomposition of liquid 2,4,6-trinitrotoluene (TNT), and its ~~2,4,6~~-trimethyl labeled analogue (TNT-d₃) I.[1] This study integrated the condensed phase DIE approach with isothermal differential scanning calorimetry (IDSC) and identified the pendant methyl group C-H bond rupture as the rate-controlling feature which initiated TNT's autocatalytic decomposition.[1] Very early in the TNT decomposition process, a small amount of product forms from the original TNT via the rate-limiting methyl C-H bond rupture (1° DIE), and upon reaching a threshold concentration in the liquid TNT melt, initiates TNT's autocatalytic exothermic decomposition. To obtain this result,

(2) The 1.8 to 1.4 DIE range represents an area of potential overlap for the minimum 1° DIE and maximum 2° DIE values at near ambient temperature reaction conditions. Some 1° DIEs with a ratio less than 1.4 have been observed as well as 2° DIEs above this value. A value above 2.5 has been suggested as definitely reflecting a 1° DIE at more normal reaction temperatures. But, both 1° and 2° DIE values are normally decreased with significant temperature increases. Because of the very high temperatures encountered in the exothermic events discussed, a 2° DIE value in the upper regime is unlikely, while a true 1° DIE value would be expected to function near the minimum high temperature value. Past studies showing a confirmed 1° DIE equal to 1.66 for TNT decomposition within a 245-269°C temperature range and another decomposition product analysis study with nitamines,[15] also tends to support this contention about lower 1.35-1.41 values representing 1° DIE effect.

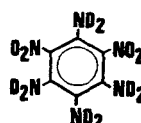
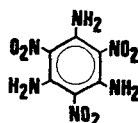
inverse induction ratios (t_D/t_H) were shown to be a valid DIE measurement since rate constant time ratios (k_H/k_D) are unavailable.[1] The same IDSC method subsequently revealed that TATB, II, solid state decomposition is likely controlled by a rate-limiting pendant amino group N-H bond rupture (1° DIE) during the first stage of its two-stage decomposition process.[2] The compound,



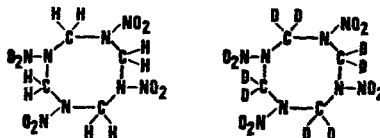
I



II



octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) III, represents the first nitramine to be investigated using the condensed phase DIE approach with IDSC.[3] The highly controversial HMX decomposition process surprisingly produced three



III

distinct DIE values when analyzed several degrees below its melting point. These three DIE values were found to be dependent upon the predominant physical state of HMX during various portions of the decomposition process (Figure 3).

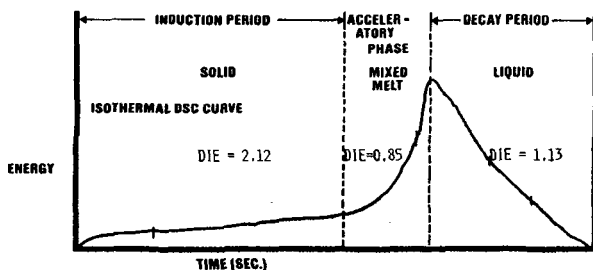
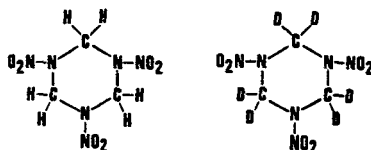


Figure 3

Initially HMX decomposition in the solid state produced a 1° DIE indicating kinetic C-H bond rupture as the rate-controlling mechanistic feature. A separate rapid heating isothermal pyroprobe degradation (IPD) of HMX 21°C below its melting point also produced a 1° DIE during an instantaneous conversion of solid HMX to gaseous products and further verified solid state C-H bond rupture as controlling HMX decomposition in this phase.[3] Still further verification came from a later isothermal thermal gravimetric analysis (TGA) study which also produced a 1° DIE [4] consistent with a solid state HMX C-H bond rupture controlled mechanism.[3] Once melting began, HMX entered a mixed-melt phase and produced an inverse DIE, indicating a contraction of C-H bonds from an increase in bond force constant; this possibly is caused by its rigid solid state hydrogen bonds being weakened during melting. Momentarily, the rate at which physicochemical microscopic crystal lattice forces are overcome in the liquefaction seems to control the HMX

decomposition process until complete melting is achieved.[3] Liquid state HMX decomposition produced a 2° DIE and ultimately showed covalent ring C-N bond rupture to be the rate-controlling mechanism in this phase of the decomposition process.[3] The six-membered nitramine cousin of HMX, RDX IV, has most recently been studied in its decomposition mode using the condensed phase DIE approach with both isothermal TGA[4,7] and IDSC[5,6] methods. The published TGA investigation



IV

apparently measured the RDX/RDX-d₆ DIE value in the liquid state,[4,7] and provides data very similar to that observed in a preliminary IDSC study conducted with RDX solely in the liquid state.[5,6] Both suggest the liquid state RDX decomposition process is controlled by a kinetic rate-limiting C-H bond rupture mechanism. Table I summarizes the slow decomposition DIE results obtained for four energetic compounds using the three ambient pressure isothermal analysis methods mentioned. Of special note is the different rate-controlling kinetic mechanism in HMX (ring C-N bond rupture) and RDX (C-H bond rupture) when both are in the liquid state, while solid state HMX decomposition occurs by the same mechanism as liquid RDX decomposition. The reasons for these differences from two compounds of similar molecular structure is not yet understood.

Table I. Condensed Phase Slow Decomposition Deuterium Isotope Effects

Compound (Phase)	DIE (type)	Rate-Controlling Step	Method	Reference
TNT (liquid)	1.66 (1°)	Methyl C-H Rupture	IDSC	1
TATB (solid)	1.5 (1°)	Amino N-H Rupture	IDSC	2
RDX (?)	1.50 (1°)	C-H Rupture	TGA	4,7
(liquid)	1.7-2.1 (1°)	C-H Rupture	IDSC	5,6
HMX (solid)	2.21 (1°)	C-H Rupture	IDSC	3
(solid)	3.04 (1°)	C-H Rupture	IPD	3
(mix. melt)	0.85 (inv)	Intermol. Lattice Forces	IDSC	3
(liquid)	1.13 (2°)	Ring C-N Rupture	IDSC	3
(?)	1.91-2.07(1°)	C-H Rupture	TGA	4

Three major points arise from the condensed phase DIE investigation of the HMX slow decomposition.[3] First, the slow decomposition event does not possess a single, unique rate-controlling mechanism; rather, it is a chemical process constituting at least three potentially rate-controlling mechanistic pathways. Secondly, the microscopic rate-limiting mechanistic pathway in HMX decomposition is dependent upon the predominant macroscopic physical state which exists during the occurrence of the decomposition event. Thirdly, the predominant macroscopic physical state of the HMX decomposition is determined by the externally applied boundary conditions of the experiment and its apparatus design. These three points represent a possible bridge between microscopic condensed phase DIE-determined mechanisms followed by transient chemical species and the macroscopic properties or behavioral patterns of a compound.

Beyond ambient pressure slow decomposition and rapid pyrolysis degradation, high pressure/temperature combustion, thermal explosion and detonation events initially involve rapid thermochemical decomposition/degradation processes for producing the propagating mechanism which ultimately initiates or drives the event itself. The near ambient pressure, isothermal results displayed in Table I not only provide a mechanistic link to both the microscopic mechanistic characteristics and macroscopic behavioral features of these for more rapid and hostile energetic events; but they also provide some evidence that extrapolations from the milder decomposition/degradation regime might be carried into the more extreme events like combustion, thermal explosion, and detonation.

Combustion represents an energetic phenomenon whose temperature and pressure regimes fall between the two extremes of slow decomposition and detonation; it can also be a precursor to the latter. The combustion event has been investigated with HMX and its HMX-d₈ analogue.[8-9] Heterogeneous combustion of solid pressed HMX cylindrical pellets is comprised of two exothermic processes, and each has its own rate-limiting step. Thermochemical decomposition provides the neutral gaseous products which leave the condensed phase pellet surface and migrate into the burning zone where flame oxidation converts these transient gaseous decomposition species into final combustion products. The slower rate-limiting step of either the thermochemical decomposition or the flame oxidation processes will ultimately control the burn rate. Comparative high pressure combustion studies of identically synthesized HMX and HMX-d₈ pressed pellets were conducted in a window bomb on samples pressed to 96-97% of the HMX single crystal density. Their burn rates were determined from high speed photography run at 400 frames per second. Table II illustrates the results obtained from burn rate ratios (r_{BH}/r_{BD}) produced by the HMX/HMX-d₈ samples at various pressures. The burn rate is a

Table II. Condensed Phase Combustion Deuterium Isotope Effects

Compound	500 psig/Rate-Controlling Step	1000 psig/Rate Controlling Step
HMX	1.37/C-H bond rupture	1.60/C-H bond rupture
RDX	1.37/C-H bond rupture	1.47/C-H bond rupture

global rate, comprised of many different reaction rate constants for each component reaction step. If the single rate-limiting component reaction step is significantly slower than all the others, a DIE could appear in the overall burn rate ratio. The results in Table II demonstrate a definite DIE from burn rate ratio comparison and most likely represents a 1° DIE at both pressures. This suggests the global burn rate of HMX to be kinetically controlled between 500 psig (3.55 MPa) and 1000 psig (6.99 MPa) by covalent C-H bond rupture.[8-9] Similar results were found in a identical study of RDX and RDX-d₆ pressed pellets.[5,6] Because the decomposition rates of cyclic nitramines are known to increase in going from the solid to liquid and finally the gaseous state,[16] and because the IDSC decomposition study of HMX revealed a rate-limiting C-H bond rupture to be present only in its solid condensed phase state,[3] the overall HMX burn rate ultimately could be controlled by solid state C-H bond rupture during the condensed phase thermochemical decomposition portion of the combustion event.[8-9] A DIE outside the 1° DIE range and equal to 1.24 at 1500 psig (10.44 MPa) represents a result beyond the scope of this paper's discussion and review; it could be revealing a 2° DIE and rate-limiting mechanistic change, or a masked 1° DIE value [1,3].

The thermal explosion event is a more hostile event than combustion and also has been investigated with the condensed phase DIE approach using a series of time-to-explosion studies.[2] From this type of study, the first possible link between microscopic kinetic chemical reaction mechanisms and macroscopic energetic material sensitivity has been suggested.[2,10] During a time-to-explosion tests

in which energetic compounds are totally confined, critical temperature differences between TATB[2], DINGU[2], PETN[2], HMX[3], and their respective deuterium labeled analogues were measured; and, a possible relationship to IDSC-determined condensed phase DIE values was noted (Table III).[2,10] Compounds whose deuterium labeled analogue possess a higher critical temperature than the unlabeled material also provide a normal (1° or 2°) DIE by IDSC analysis (Table I) and tend to be more thermally stable. Unlabeled compounds which provide a critical temperature equal to or greater than their analogous deuterium labeled analogue, appear to correlate with either no DIE or an inverse DIE.

TABLE III. Deuterium Isotope Effect and Possible Sensitivity Correlation

DIE (Type)		Thermal Sensitivity (Δt_c)	Impact Sensitivity
1.5 (1°)[2]	<u>S</u>	TATB-d ₆ > TATB (12°) [2a]	
---	---	DINGU-d ₂ > DINGU (6°) [2a]	
1.66 (1°)[1]	<u>L</u>		TNT-d ₃ > TNT [12]
1.50 (1°)[4]	<u>L</u> ?		RDX-d ₆ > RDX [4a]
1.7-2.1 (1°)[5,6]	<u>L</u>		RDX-d ₆ > RDX [4a]
2.21 (1°)[3]	<u>S</u>		HMX-d ₆ > HMX [4a]
1.9-2.1 (1°)[4]	<u>S</u> ?		HMX-d ₈ > HMX [4a]
1.13 (2°)[3]	<u>L</u>		HMX-d ₈ > HMX [4a]
---	---	PETN-d ₈ = PETN (0) [2]	PETN-d ₈ = PETN [2b]
0.85 (inv.)[3]	<u>MM</u>	HMX-d ₈ < HMX-d (12°) [3a]	

[1],[2],[3] IDSC-Determined [2a][3a] Time-to Explosion Test-Determined
 [2b] Impact Weight-Determined [4] TGA-Determined
 [4a],[11] Exploding Foil Impact-Determined

S = solid L = liquid MM = mixed melt

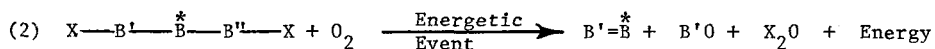
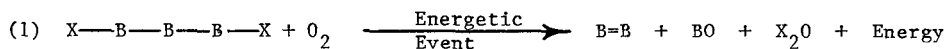
From the macroscopic critical temperature results (t_c) with TATB ($t_c=354^\circ\text{C}$) and TATB-d₆ ($t_c=366^\circ\text{C}$), a 1° DIE rate-limiting microscopic amino N-H bond rupture not only appears to control its ambient pressure slow decomposition process (Table I and III), but apparently is a significant rate-determining contributor to its pressurized self-heating process to thermal explosion.[2] The higher critical temperature of DINGU-d₂ (211°C) over DINGU (204°C) also suggests a normal (1° or 2°) DIE in the kinetically controlled reaction mechanism driving its self-heating to explosion process. The far more sensitive PETN compound, however displays no critical temperature difference ($t_c = 183^\circ\text{C}$) and suggests the absence of a kinetically controlled rate-limiting chemical mechanism in its self-heating process (Table III). This lack of a microscopic kinetic rate-controlling mechanism in PETN's thermal explosion event is further demonstrated by its displaying no sensitivity difference to impact initiation and possibly suggests a link between a condensed phase kinetic DIE-determined microscopic rate-limiting reaction step and the macroscopic shock sensitivity behavior of a given energetic material.[2]

The HMX and HMX-d₈ time-to-explosion results (Table III) further support this premise of a possible microscopic DIE effect and macroscopic sensitivity correlation.[3] In the confined sample boundary conditions imposed by the time-to-explosion test itself, the gaseous decomposition gases remain in an intimate interaction with the solid HMX, or HMX-d₈, and probably cause a resultant physicochemical melting point depression. This rapidly advances the HMX compound into a predominantly mixed melt state just prior to the moment of the thermal explosion event. The higher thermal sensitivity of HMX-d₈ ($t_c=242^\circ\text{C}$) compared to the more stable normal HMX($t_c=257^\circ\text{C}$) analogue, suggests the self heating to explosion process occurs more rapidly with HMX-d₈ than in normal HMX. Such a kinetic result correlates directly with the inverse DIE observed in the HMX mixed melt state (IDSC analysis) where HMX decomposition was the most severe (Figure 3).[3] This correlation suggests a further bridge between a microscopic DIE-determined rate-limiting mechanism and its macroscopic critical temperature

and thermal explosion sensitivity features. The possible relationship between energetic compound explosive sensitivity as revealed by its critical temperature, and the type of DIE shown by IDSC analysis was first proposed to result from a compound's inherent volume of activation ($\Delta V^\ddagger$) during explosive initiation.[2] A less sensitive compound's deuterium labeled analogue provides a higher critical temperature and a normal DIE (1° or 2°). This results from a slower kinetically controlled rate-limiting mechanism which propagates the chemical process to the explosion event less rapidly than with the unlabeled analogue. A normal DIE proceeds through a microscopic transition state in which the labeled covalent bonds are lengthening and creating a larger volume during activation. An increased pressure on this expanding volume during activation, either by gaseous product confinement (time-to-explosion test) or by a shock front (impact weight), would inhibit the explosive event from proceeding and would correlate to a less sensitive compound's macroscopic behavior.[2] Conversely, an inverse DIE indicating a labeled covalent bond contraction and resultant decrease in transition state volume during activation, would be accelerated by an increase in pressure to an explosion event. This situation characterizes the macroscopic behavior of a more sensitive explosive compound.[2] While this possible correlation of the microscopic DIE determined rate-controlling mechanism with a compound's macroscopic relative sensitivity behavior is not yet complete, there is enough preliminary evidence to consider this possibility. The remaining data displayed in Table III is gathered from more recent impact sensitivity studies [4,11] on other compounds known to exhibit isothermal IDSC- or TGA-determined condensed phase DIEs; and, it further supports this hypothesis. Using the exploding foil method,[4] a slightly lower macroscopic impact sensitivity, was displayed by the more stable deuterium analogues of TNT, RDX, and HMX, each of which afford a microscopic normal (1° or 2°) DIE during slow decomposition.[1,3-6] A 1° DIE results in HMX solid state decomposition and a 2° DIE when occurring in the liquid phase.[3] The increased impact initiation stability of TNT- d_3 over TNT and of RDX- d_6 over RDX, imply a normal DIE and further suggest that the same kinetically controlled rate-limiting C-H bond rupture mechanism observed in slow decomposition may regulate the process leading to the detonation event.[4,11] The quadruple entry of HMX in Table III could, at first glance, appear contradictory. However, it might well be expected when one considers the initial DIE investigation with HMX and HMX- d_8 where a mechanistic dependence upon physical state was found and variance of the predominant physical state with external experimental boundary conditions was demonstrated.[3] The HMX data found in Table III possibly reveals that HMX thermal sensitivity is affected by the microscopic physicochemical rate-limiting intermolecular lattice forces of the mixed melt phase (inverse DIE) and by the macroscopic sample confinement imposed by the boundary conditions of the time-to-explosion test. HMX impact sensitivity apparently is affected by a different microscopic kinetic rate-limiting mechanism, possibly solid state C-H bond rupture, where macroscopic sample confinement may not be as severe, and where time is insufficient for the product gases generated to produce a rapid melting point lowering into the mixed melt phase. In this case, the HMX may still predominantly exist in the solid state and be controlled by solid state C-H bond rupture. Quite possibly, then, different rate-controlling mechanisms are propagating the processes leading to the HMX thermally-initiated explosion and impact-initiated detonation events.

Isotopic Product Exchange (IPE). The isotopic product exchange approach has been used sparingly for investigating the mechanistic pathway of an energetic material's energy releasing process during a given type of exothermic event. Unlike the condensed phase DIE, the IPE approach is quite expensive to use; but like the complementary DIE approach, it can provide unique microscopic information on transient species behavior which currently cannot be obtained by other approaches. The IPE approach normally uses isotopes (^{13}C , ^{15}N , ^{18}O) other than those of hydrogen (ie. deuterium, tritium) where selected atoms are displaced in an energetic compound by their only slightly heavier nuclei. Mass spectrometry detection of labeled (*) and unlabeled nuclei ratios (ie. C/C, N/N, O/O) in reaction products after the exothermic event, reveals which bonds of the original compound are actually ruptured during the event and quantify the extent to which

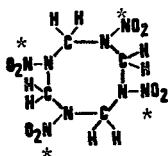
they are retained in the final products. In cases where two energetic compounds are present in a single, mixed sample, the IPE technique can show the degree to which transient species from the individual component chemical processes of each initial compound interact with one another during the event. The hypothetical compound, B_3X_2 , (Equation 1) produces three products during an energetic event



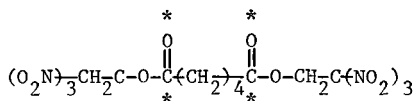
* Labeled Nuclei		* B=B''	* B'O	
		B'≡B''	B''O	
B/B = 2.0	→	2.0	2.0	Random B/B Exchange with <u>some</u> B ₂
B/B = 2.0	→	1.0	0	Total B-B Retention with <u>no</u> B ₂

which could be a decomposition, combustion, thermal explosion, or detonation. Collection and analysis of the three products reveal that all B-X bonds have ruptured since no BX_2 product is found. The unlabeled B_3X_2 compound, however, reveals nothing about the extent to which the B-B bonds are ruptured. Therefore, one cannot determine whether the chemical mechanism operating in this energetic event's energy-releasing process occurs by a completely random fashion with the rupture of all bonds contained in the original B_3X_2 compound, or whether some B-B bond retention occurs during B_2 product formation. A mass spectrometric analysis of the B/B ratio in the B_2 and BO products (Equation 2) would determine if random B/B nuclei exchange occurred. In this case B/B would be 2.0, the same as in the labeled B_3X_2 reactant; and, all chemical bonds including both B-B bonds, would have ruptured to form individual transient atomic species (B and X) which randomly reacted with O_2 to produce BO and X_2O as well as statistically random, B_2 recombination. If a B/B ratio for B_2 and BO are found to be 1.0 and 0 respectively, a diffusion control is demonstrated where a B-B bond was always retained providing a molecular B-B transient species which did not react with O_2 , plus an accompanying unlabeled B atom which forms BO. At no time would both B-B bonds simultaneously rupture to produce three atomic B species from molecule of B_3X_2 . A B/B ratio for the two B-containing products of intermediate value would signify some degree of limited B-B bond retention and diffusion control, and would quantify its extent.

The first mechanistic application of the IPE approach with an energetic explosive material was reported for the slow decomposition of HMX and its nitro-¹⁵N-labeled analogue V.[17] This investigation suggested that an N-NO₂ bond rupture mechanism did not occur to a significant extent in this decomposition event's energy-releasing process because 99% of the N₂O decomposition product found carried a ¹⁵N NO labeling. However, some unlabeled HCN product was also detected which had to result from a portion of the unlabeled HMX ring structure following a small amount of N-NO₂ bond rupture. The nature of the IPE approach does not provide a method for identifying a rate-controlling step,[17] but the complementary condensed phase DIE approach does.[1] Integration of this IPE study of HMX decomposition [17] with the recent condensed phase DIE investigation [3] is discussed in the next section.



V



VI

Two IPE investigations have been conducted with the detonation event using both a pure explosive compound and a two-component formulation.[18] The detonation event of both the homogeneous, single explosive compound, bis-(2,2,2-trinitroethyl) adipate, and the heterogeneous, non-ideal Amatol 20/80 formulation was conducted under vacuum conditions in a detonation calorimeter. The experimental design precluded detonation product re-equilibration from reflected shock waves rebounding off the calorimeter inner walls. The detonation products were collected and analyzed by mass spectrometry to determine the unlabeled/labeled nuclei ratios in key reaction products (Table IV).

Table IV BTNEA and Detonation Product Isotopic Ratios [18]

Compound	$^{12}\text{C}/^{13}\text{C}$	$^{16}\text{O}/^{18}\text{O}$
BTNEA	4.8	11.7
CO	4.8	11.2
CO ₂	4.7	11.4
CH ₄	4.5	—
C (solid)	4.6	—

The homogeneous BTNEA, VI energetic compound contained ^{13}C and ^{18}O labeled nuclei in the carbonyl moiety of the molecule, and, in a sense, had its structure isotopically labeled to favor retention of its $\text{C}=\text{O}$ labeled bond in the CO and CO₂ detonation products. Despite this favored microscopic isotope labeling feature in the BTNEA, all chemical bonds were ruptured during its detonation and formed atomized transient reactive species. These species attained a complete steady-state thermodynamic equilibrium in the detonation wave front and recombined in a statistically random fashion prior to kinetic freeze out as the isolated detonation products. As shown by Table IV, diffusion on a molecular level cannot be an important rate-controlling process for this homogeneous explosive event.[18] The $^{12}\text{C}/^{13}\text{C}$ and $^{16}\text{O}/^{18}\text{O}$ ratios are essentially the same for all products as for the original BTNEA molecule. Based upon the degree of ^{13}C and ^{18}O labeled nuclei incorporated into the original BTNEA compound, a $^{12}\text{C}/^{13}\text{C}$ ratio equal to 3.79 would have resulted for both CO and CO₂ if the carbonyl moiety's bonds were retained in formation of these structurally analogous CO and CO₂ products; additionally, no ^{13}C would have been found in either the methane, CH₄, or solid carbon products. The ratio for the CH₄ and solid C products is especially noteworthy since only a 10% bond retention would have yielded a $^{12}\text{C}/^{13}\text{C}$ ratio equal to 5.5.[18]

A heterogeneous, two-component Amatol 20/80 weight composition: [20% ammonium nitrate (AN)/80% 2,4,6-trinitrotoluene (TNT) by weight] explosive formulation was also examined by this IPE approach using the same detonation calorimetry method.[18] This non-ideal behaving AN/TNT binary explosive had the AN compound labeled with ^{15}N nuclei on both its ammonium and nitrate ions while the nitrogen nuclei in the TNT molecule's nitro-groups remained as normal ^{14}N nuclei. The amount of ^{15}N enrichment in the Amatol 20/80 compound provided 1.774 g-atoms/mol ^{14}N and 0.818-atoms/mol of ^{15}N nuclei. Table V displays the results obtained when the nitrogen gas (N₂) product from Amatol 20/80 detonation was collected and analyzed. Only a small degree of nitrogen atom exchange occurred between the ^{15}N nuclei of the AN and the ^{14}N nuclei of TNT in producing the N₂ detonation product. The actual numbers are far from a statistically random 100% mixing of transient

species and represent only a 12% mixing when one assumes each compound's (AN and TNT) degradation occurs independently behind the shock front.[18] This result, which quantifies the microscopic diffusion control mechanism present in Amatol's non-ideal energy releasing process during its detonation event, exhibits a significant reason why one observes macroscopic non-ideal behavior with this heterogeneous explosive. Microscopic diffusion control limits the exothermic reactions of transient, chemical species, and in doing so, results in an energy releasing process which provides macroscopic explosive performance measurements well below the calculated ideal output. This IPE approach also provided the necessary data to determine the unmeasurable microscopic diffusion layer thickness. From the 12 percent isotopic mixing value and measured particle size distribution in the initial Amatol explosive, an effective diffusion layer thickness equal to $0.6 \mu\text{m}$ was calculated.[18]

Table V Amatol 20/80 Nitrogen Product Isotopic Distribution [18]

Amatol 20/80: 20% $\text{NH}_4^* \text{NO}_3^*$ (^{15}N enriched)/80% TNT (All ^{14}N nuclei)

N_2 Product: g-atom per mol Amatol 20/80

(100% mixing) (actual mixing) (0% mixing)

$^{15}\text{N}-^{15}\text{N}$	0.086	0.333	0.409
$^{15}\text{N}-^{14}\text{N}$	0.645	0.085	0
$^{14}\text{N}-^{14}\text{N}$	0.564	0.687	0.887

Condensed Phase DIE and IPE Correlation. Earlier mention was made of a condensed phase DIE [3] and IPE[17] thermochemical decomposition both conducted in a similar temperature range on HMX. The initial IPE investigation conducted at temperatures ranging from 230°C to 285°C revealed large amounts of N_2O and CH_2O (formaldehyde) products. Most of the N_2O (99%) retained the $^{14}\text{N}-^{15}\text{N}$ isotopic label of the initial nitro- ^{15}N labeled HMX molecule V. The results for this IPE experiment (Table VI) were consistent with a simple concerted mechanistic decomposition pathway which produces three molecules of $\text{CH}_2=\text{N}-^{15}\text{NO}_2$ that further decompose into CH_2O and $^{14}\text{N}-^{15}\text{N}$. A small amount of unlabeled HCN was found, but the results strongly suggested $\text{N}-\text{NO}_2$ bond rupture did not occur to a significant extent; but the IPE approach itself could not permit any clear conclusion about the rate-controlling step of this decomposition.[17] Information regarding the rate limiting step comes from the complementary condensed phase DIE investigation.[3] The surprising indication that at least three phase-dependent rate-controlling steps describe potential mechanistic pathways of HMX's energy release process during its decomposition event reveal a far more complex situation. The DIE approach coupled with other non-labeled HMX decomposition product studies leads to a more complex but unified mechanistic model.[3] This model describes an initial NO_2 radical formation from $\text{N}-\text{NO}_2$ bond rupture; this reactive radical then abstracts a hydrogen atom from HMX to form HONO and causes the rate-limiting $\text{C}-\text{H}$ bond rupture. The remaining HMX radical decomposes further to provide an HCN molecule from the HMX ring structure, plus three molecules of both N_2O , derived via $\text{N}-\text{NO}_2$ bond retention, and CH_2O . Decomposition of the unstable HONO molecule provides oxidizer and catalytic species including NO , which attack other HMX molecules and predominantly provide more N_2O and CH_2O products, especially when the mixed melt or liquid state is encountered. While initial $\text{N}-\text{NO}_2$ bond rupture and the small amount of resultant HCN product are not major mechanistic features by the IPE approach in HMX's decomposition event, it appears to be a major player in terms of initiating the overall exothermic process and provides its rate-controlling step.[3,6,15] When one follows through the mechanistically unified exothermic process proposed for the thermochemical decomposition event by a graphic representation in reference 3, the results predicted by the DIE-generated mechanism[3] are consistent with the IPE study [17] for an HMX molecule with ^{15}N

labeled nitro groups, V. Table VI compares the actual IPE [17] and predicted DIE [3] results and demonstrates the complementary mechanistic correlation both approaches provide for this exothermic event.

Table VI. Comparison of IPE and DIE Mechanism Data

IPE Experimental Results (t=230-285°C) [17] DIE Mechanism Results (t=278-280°C) [3]

Product	<u>Actual</u> Isotopic Exchange	<u>Predicted</u> Isotopic Exchange
N ₂ O	* NNO 99%	100%
	** NNO 1%	0
HCN	* HCN 0	0
	HCN 100	100
NO	* NO 100	100
	NO 0	0
N ₂	* N=N 100	-

CONCLUSION

Two kinds of complementary isotopic labeling approaches have been employed to elucidate, in-situ, the key microscopic mechanism followed by the energy releasing processes of various exothermic events. Condensed phase deuterium isotope effect (DIE) and isotopic product exchange (IPE) approaches have successfully described the mechanistic behavior of microscopic transient chemical species as they participate in the energy releasing processes which initiate or drive exothermic high energy decomposition, combustion, thermal explosion, and detonation events. The condensed phase DIE describes the kinetic limitations which may control an exothermic event's global energy release rate and selectively can determine the specific covalent chemical bond rupture responsible. Additionally, it can help bridge the relationship existing between microscopic molecular reaction mechanisms and physical macroscopic behavioral properties or performance. The IPE approach complements the DIE technique by identifying the mechanistic pathway by which covalent bonds rupture and produce the transient reactive species that reform into final products, and in doing so, can reveal whether a given high energy event's exothermic process is diffusion controlled at the microscopic level. The IPE approach also provides a link between macroscopic material composition or performance factors and the microscopic mechanism which is followed. Sufficient data has been gathered by these two in-situ approaches on a number of high energy events to suggest some definite correlation between microscopic molecular mechanisms and macroscopic behavioral features which can guide future research attempts to more fully elucidate the nature of high energy events produced by energetic materials.

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Question - J. DANGREAU

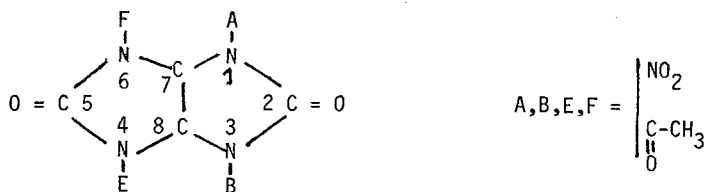
In describing experiments with amatol, you have found that diffusion was a controlling factor of reaction. I suppose you were speaking of diffusion of N_2 ?

Réponse -

Yes. The reference describing this novel experiment is : R.R. McGuire, D.L. Ornallas, I.B. Akst, *Propellants and Explosives*, 4, 23 (1979). The authors show only a 12% mixing of atoms to form the ^{15}N ^{14}N labeled detonation product from as Amatol 20-80 (20 AN/80 TNT by weight) where both nitrogen atoms on AN (NH_4NO_3) are ^{15}N and all nitro nitrogen atoms on TNT are unlabeled (^{14}N). The authors attribute this low 12% mixing to a diffusion controlled process where the ^{15}N atoms from labeled AN and ^{14}N atoms from normal TNT do not significantly interact because of each compound independently undergoing its own separate reaction in the shock front. Another possibility could exist. Perhaps the mixing of AN and TNT derived transient species is not diffusion controlled, but the kinetics of the intermolecular reactions proceed more slowly than the reaction time provided by the detonation event. If this be the case, the detonation phenomena would be kinetically controlled. I assume the authors discounted this possibility because of the homogeneous BTNEA explosive showing no kinetic control in its detonation event. Only the N_2 product was analyzed in this study. Thank you for your interest and question.

Question - J. BOILEAU

On pourrait peut-être appliquer la méthode de IDSC au DADN et au trinitro monoacétyl dérivé de l'octogène pour voir à partir de quand s'affaiblissent les liaisons C-N ou NNO_2 par rapport à CH. De même sur les dinitrodiaétylglycoluriles 1,4 ; 1,3 ; 1,6 ; dont on sait par structure aux rayons X et réactivité les modifications de forces de liaisons en fonction des positions relatives des groupes NO_2 par rapport au plan des noyaux. (Peut-être avec $^{13}COCH_3$?)



Réponse -

Unfortunately the deuterium isotope effect method would not be the best suited one for any of the three cases mentioned. Since it measures only the slowest rate-limiting bond rupture, it reveals little about the bond strength of the other bonds in a molecule. In the case of a DADN/DADN-dg comparison, one would find out if C-H (1° DIE) or C-N bond (2° DIE) rupture was rate limiting. If a 2° DIE was observed, a simultaneous product analysis would be necessary to determine if it was the ring C-N bond or the acetyl C-N bond which was producing it, and at what point in the bond rupture sequence it occurred. Rupture of a molecule's weakest bond (faster reaction) does not produce a DIE. In the DADN case, isotopic product exchange (IPE) could be used if the products were collected and analyzed by glpc/mass spectrometry where ^{15}N nitro groups are incorporated into the DADN. The same IPE approach might provide some useful data for SEX (trinitromono-acetyl

compound). A useful reference might be S. Bulusu and J.R. Autera, Chem. and Indust., 2177 (1967). For the DINGU problem, isothermal DSC would most likely not be sensitive enough to detect the DIE which might be caused by a $^{13}\text{COCH}_3/\text{COCH}_3$ comparison if the N-COCH₃ bond were the slowest (strongest bond) rupture in the DINGU derivatives you mentioned. Kinetic $^{13}\text{C}/^{12}\text{C}$ isotope effects range only from 1.02 to 1.10 in carefully controlled reactions conducted in solution. It might be possible to do a $^{13}\text{C}/^{12}\text{C}$ study in a mixed acid nitration media, and this possible could reveal if N-COCH₃ bond rupture is the slow rate-limiting step in various diacetyl DINGU isomer (1,4 ; 1,3 ; 1,6) nitrations. Thank you for your interest and question on this.

Question - S. ODIOT

What more information on thermosensitivity and isotopic effect ? PETN TNT..

Réponse -

The transparency copies I used in the talk at the workshop plus the manuscript on pages 6-8 can provide you the additional information you request. There appears to be a relationship between the type of DIE found by isothermal decomposition studies and with either thermal or shock sensitivity, but more systematic and detailed investigations are needed to establish a definite correlation. Thank you for your interest and question on this.