

**COMPARATIVE MECHANISTIC THERMOCHEMICAL
DECOMPOSITION ANALYSES OF LIQUID
HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE (RDX) USING
THE KINETIC DEUTERIUM ISOTOPE EFFECT APPROACH ***

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ABSTRACT

The condensed phase kinetic deuterium isotope effect (KDIE) approach is applied to the thermochemical decomposition of liquid RDX and RDX- d_6 using two dissimilar thermal analysis techniques. Comparative KDIE results from isothermal differential scanning calorimetry (IDSC) and from direct RDX concentration depletion measurements by quenched UV spectrometric analysis confirm the proposed proportionality between IDSC heat evolution rates and the RDX concentration depletion rate. Additionally, these KDIE data verify the proposed rate-controlling mechanistic step previously reported from an isothermal thermogravimetric investigation of liquid RDX determined from weight loss rates. Observed mechanistic and kinetic differences between the cyclic six-membered RDX decomposition and its eight-membered HMX homologue are outlined.

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INTRODUCTION

Because the thermally initiated decomposition of an organic compound can be an extremely complex process, involving numerous sequential and parallel chemical reactions, a complete mechanistic description presents a difficult problem. An especially complex challenge comes from mechanistic investigations conducted on the thermochemical decomposition process followed by the energetic compounds used as ingredients in propellant, or explosive formulations, such as the energetic cyclic nitramine homologues hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetra-nitro-1,3,5,7-tetrazocine (HMX) [1,2]. One recent mechanistic approach successfully uses the condensed phase kinetic deuterium isotope effect (KDIE) (also referred to in the literature as DKIE, DIE and KIE) for directly identifying the rate-controlling mechanistic step in the decomposition process of an energetic compound [3–9]. This key rate-controlling step usually results from a specific covalent bond dissociation and is responsible for regulating the global energy release rate of an energetic compound during its decomposition. The importance of this rate-controlling step is reflected in recent mechanistic KDIE investigations which have been extended into progressively higher order pressure, temperature and rate regimes. Such studies reveal that the same rate-controlling mechanistic step which regulates its thermochemical decomposition process at atmospheric pressure, also can exist in the pyrolytic deflagration [8] of an energetic compound as well as in its combustion [6,7,10–12], thermal explosion [5,8], and possibly, detonation [9,13] phenomena.

Reported here is a condensed phase KDIE investigation of the liquid phase RDX thermochemical decomposition process using two dissimilar isothermal analysis methods at atmospheric pressure. The KDIE obtained by isothermal differential scanning calorimetry (IDSC) analysis with liquid RDX and its perdeuterio RDX- d_6 analogue are compared with the KDIE found by direct UV absorbance (QUVA) concentration measurements taken on sequentially quenched liquid RDX and RDX- d_6 samples. While both methods provide a similar primary KDIE (1° KDIE) value and verify that covalent carbon-hydrogen bond dissociation probably constitutes liquid RDX's rate-controlling mechanistic step [9], this close agreement also experimentally confirms two important thermal analysis concepts. Firstly, the IDSC heat evolution rate indeed is directly proportional [14] to the global chemical reactions driving the decomposition rate of an energetic compound; and secondly, the observed KDIE produced by IDSC analysis results primarily from chemical reaction rate differences and not from variations of inherent physical properties or extraneous thermophysical effects in RDX and RDX- d_6 . This is especially true when the decomposition products of an energetic compound are primarily gaseous species [3,8]. These KDIE results are also compared with those previously reported in a

thermogravimetric analysis (TGA) study of RDX and RDX- d_6 weight loss rates [9]. Finally, the IDSC and QUVA results discussed are contrasted with those reported for the larger, eight-membered HMX homologue [8] of the structurally smaller, six-membered RDX nitramine.

EXPERIMENTAL

CAUTION: RDX is a high explosive material more powerful than TNT. Care should be taken to use proper laboratory shielding and safety procedures in all handling operations. Glassware and associated hardware should be free of scratches or jagged, sharp edges, and Teflon or plastic stirring rods and spatulas should be used to avoid static discharge to solid RDX samples which could cause accidental initiation.

The RDX and RDX- d_6 samples were prepared in an identical manner using paraformaldehyde or paraformaldehyde- d_2 [15–17] to ensure that any differences observed result solely from the deuterium isotope substitution and not from sample purity or history. The synthesis route chosen produces HMX-free RDX product; ^1H FT-NMR analysis showed the RDX- d_6 to be 98% deuterated. The ^1H FT-NMR spectra were taken on a JEOL FX90Q 90 MHz spectrometer. Melting points (uncorrected) were taken with a Thomas–Hoover unimelt melting point apparatus using unsealed glass capillary melting point tubes. All chemicals were reagent grade; no further purification was needed.

Hexamethylenetetramine (HMTA) and HMTA- d_{12} synthesis [15]

Both the HMTA and HMTA- d_{12} starting materials were synthesized by reacting NH_4OH (28.0–30.0% NH_3) with paraformaldehyde or paraformaldehyde- d_2 respectively, using the reported procedures [15] with several slight modifications [8,12].

Hexahydro-1,3,5-triacetyl-1,3,5-triazine (TRAT) and TRAT- d_6 synthesis [16]

To 33.2 g (361 mmol) acetic anhydride stirred with a Teflon-coated magnetic stir bar at room temperature, 8.3 g (59 mmol) HMTA was added. The solution was heated at 98°C for 2 h and then cooled to 5°C before 20 ml H_2O was added. The solution was then stirred for an additional 30 min at 5°C. Vacuum distillation produced a viscous yellow oil to which 20 ml H_2O was added. The mixture was cooled to induce precipitation. The solid was filtered and dried under vacuum over NaOH pellets to yield 8.65 g (68%) product; m.p. 96°C; ^1H FT-NMR (DMSO- d_6) δ 2.1 (singlet), δ 5.2 (singlet). TRAT- d_6 was synthesized in an identical manner using 8.3 g

HMTA- d_{12} to yield 8.56 g (68%) TRAT- d_6 ; m.p. 96°C (sharp); ^1H FT-NMR comparison of the δ 2.1 acetal protons with the δ 5.2 methylene signal showed greater than 98% isotopic purity on the methylene ring sites.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and RDX- d_6 synthesis [17]

Under dry nitrogen, a 100 ml three-necked round bottom flask was charged with 4.0 g (28 mmol) P_2O_5 and a Teflon-coated magnetic stirring bar; the flask was then fitted with a reflux condenser in one neck and a thermometer in a second neck to monitor the reaction temperature. The 24/40 reaction flask neck was stoppered using a pressure-equalized addition funnel and 12 g (190 mmol) anhydrous HNO_3 was added dropwise to the stirred solution causing the reaction to exotherm to 41°C. When the stirred solution had cooled to 35°C, 0.400 g (0.0018 mmol) TRAT was added all at once through a funnel inserted in the top of the reflux condenser. The reaction flask was then placed in an oil bath, and the reaction mixture was heated at 65°C for 15 min. The solution was allowed to cool to room temperature and was then poured onto crushed ice. The iced solution was left to stand overnight at room temperature in a fume hood or until all the ice had melted. The solid precipitate was filtered (use a porcelain Buchner funnel with filter paper pad, *not* a glass fritted Buchner funnel) and washed with deionized H_2O to yield a clean white product. Drying gave 2.98 g (71%) product; m.p. 203°C; ^1H FT-NMR (DMSO- d_6) δ 6.10 (sharp singlet). RDX- d_6 was synthesized in identical manner using 0.400 g TRAT- d_6 and yielded 0.339 g (81%) RDX- d_6 ; m.p. 203–205°C.

Isothermal DSC analysis

All IDSC measurements were made with a Perkin–Elmer DSC-4 calorimeter. RDX or RDX- d_6 were weighed into aluminum pans (Perkin–Elmer part no. 319–0264) which were topped with perforated lids containing a 0.1 mm drilled hole and then hermetically sealed. Sample size for each aluminum pan was 2.00 ± 0.04 mg for each run. The DSC instrument was calibrated at 429.78 K using an indium standard. The DSC instrument was brought to its desired temperature and after temperature equilibration the sample pan was placed in the DSC sample head; the deflection from the baseline was taken as the starting point for the IDSC scan. Data were taken from the DSC instruments using a Bascom–Turner recorder; these data were then transferred to a VAX 785 computer for processing. All IDSC runs were conducted at atmospheric pressure under a slow nitrogen gas purge atmosphere; pseudo-first order rate constants k_h and k_d were determined for RDX and RDX- d_6 samples, respectively, in order to obtain k_h/k_d -based KDIE values. At each isothermal temperature, a minimum of seven runs and a

maximum of ten runs were used to determine an averaged rate constant for the individual RDX and RDX- d_6 samples.

Isothermal decomposition UV absorption analysis

Into several Pyrex laboratory glassware 6 mm \times 50 mm micro-test-tubes (cat. no. 9820), was placed 1.0 ± 0.4 mg of either RDX or RDX- d_6 . The glass micro-test-tubes were each capped with a piece of aluminum foil loosely enough that gaseous decomposition products could escape without pushing the foil off the test tube. Each capped test-tube was then placed through a square of cardboard that contained an appropriately sized hole for the test-tube diameter, such that each tube extended to approximately two thirds of its height below the cardboard square. The RDX or RDX- d_6 containing test-tube and attached cardboard square were each immersed in a silicon oil bath maintained at 485 ± 1 K (m.p. RDX = 477 K). Upon immersion, the RDX melted and individual test-tubes were extracted at different times and immediately quenched first by ice-water immersion and then immersion in liquid nitrogen. When all test-tubes were quenched, the test-tube samples were individually dissolved in CH_3CN and diluted to 10 ml. Any small amounts of condensate on the walls of the test tube were dissolved into a CH_3CN solution preparation along with the solid decomposed residue in the bottom of the test tube. The UV-spectrum for undecomposed RDX was monitored at 236 nm [18] and the concentration of remaining RDX in each sample was determined using Beer's Law and an extinction coefficient of $11275 \pm 338 \text{ l cm}^{-1} \text{ mol}^{-1}$ (lit. $10880 \pm 217 \text{ l cm}^{-1} \text{ mol}^{-1}$ for RDX [19]) derived from a sample of known RDX concentration.

RESULTS

IDSC thermochemical decomposition analysis

Under the experimental conditions used, RDX and RDX- d_6 show no early induction period (Fig. 1) as did liquid 2,4,6-trinitrotoluene (TNT) [3], 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) [4], and the KDIE physical state dependent HMX [6,8] in previously reported IDSC mechanistic KDIE investigations. Therefore, decay phase kinetics were used for determining the RDX and RDX- d_6 pseudo-first order rate constants (Fig. 2). The KDIE then was calculated at three different temperatures between 500 and 515 K (m.p. RDX = 477 K) using the k_h/k_d rate constant ratio at each temperature (Table 1). The decomposition rate increases with higher temperature as shown by the increasing slope in the decay phase portion of the decomposition curve (Fig. 3) and resembles that reported earlier for liquid RDX [20]. Within this temperature range investigated, the RDX samples have already

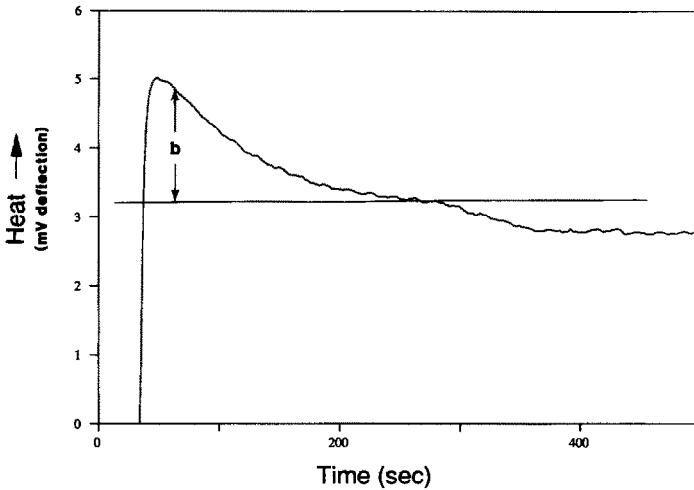


Fig. 1. IDSC thermochemical decomposition curve of RDX (505 K).

entered the exothermic acceleratory portion of the IDSC thermochemical decomposition curve by the time the sample thermally equilibrates to the preset isothermal IDSC temperature. Attempts to conduct solid state analyses several degrees below the RDX melting point were unsuccessful even though it had previously been accomplished with RDX's higher HMX homologue [6,8]. Because the solid state RDX decomposition would not produce an eventual exothermic acceleratory phase, a KDIE could not be determined using an induction time ratio (t_{id}/t_{ih}) [3,8]. Figure 4 exemplifies the decomposition rate difference between RDX and RDX- d_6 caused by the observed

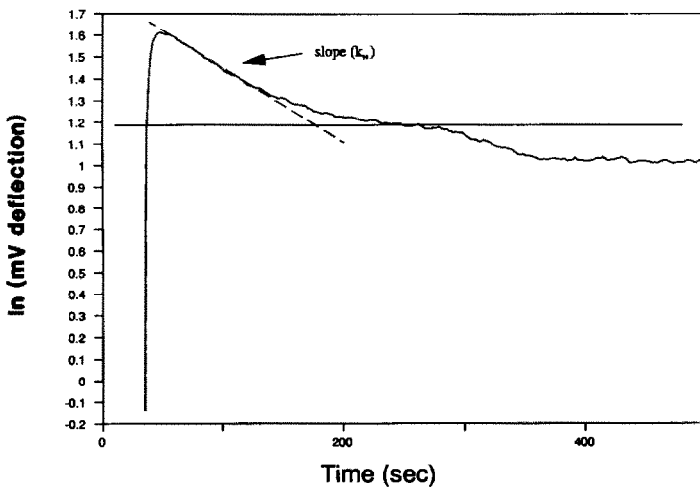


Fig. 2. IDSC pseudo-first order kinetics plot of RDX (505 K).

TABLE 1
IDSC thermochemical decomposition results

Temp. (K)	RDX k_h (s^{-1})	RDX- d_6 (s^{-1})	KDIE	
			k_h/k_d ^a	298 K
500	-0.0114	-0.00632	1.80 ± 0.18	3.84
505	-0.0136	-0.00817	1.66 ± 0.17	3.58
515	-0.0167	-0.0114	1.46 ± 0.17	3.22
			1.64 ± 0.10 ^b	3.55 ^b

^a Deviations are reported to the 95% confidence level.

^b Average value.

KDIE at all three temperatures (Table 1). The k_h and k_d rate constants shown in Table 1 are obtained by plotting the natural logarithm of the IDSC decomposition curve's vertical deflection (b) above the horizontal condensed phase baseline in the decay phase portion, against the decomposition time history (Fig. 5) [14]. Vapor phase RDX decomposition contributions [20] are subtracted (Fig. 5) by displacement of the baseline at the end of the condensed phase's decay phase curve. The RDX rate constants are obtained from the IDSC thermochemical decomposition curves at 500, 505 and 515 K, and the resultant k_h/k_d KDIE values are calculated. The rate constant at each RDX and RDX- d_6 temperature is an averaged value determined from a minimum of seven and a maximum of ten individual IDSC sample runs. The standard deviation at each temperature for the 7 to 10 sample runs comprising each rate constant ranged from $0.0013 s^{-1}$ (RDX, 515 K) to $0.00038 s^{-1}$ (RDX- d_6 , 500 K) with a mean of $0.00081 s^{-1}$ for all six rate

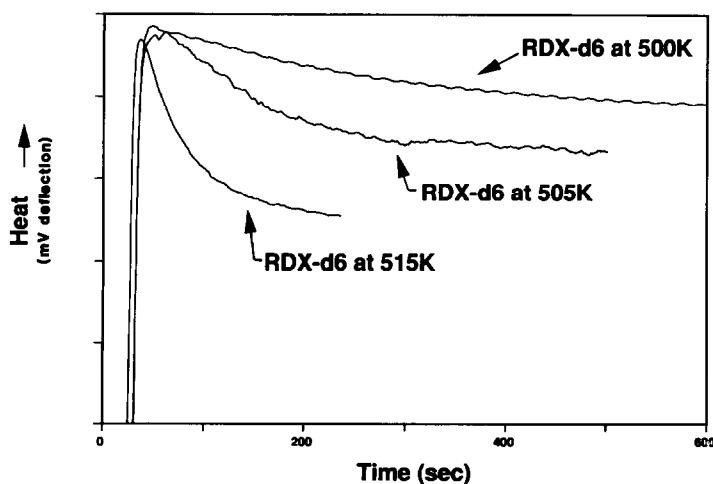


Fig. 3. IDSC thermochemical decomposition curves of RDX- d_6 (500, 505, 515 K).

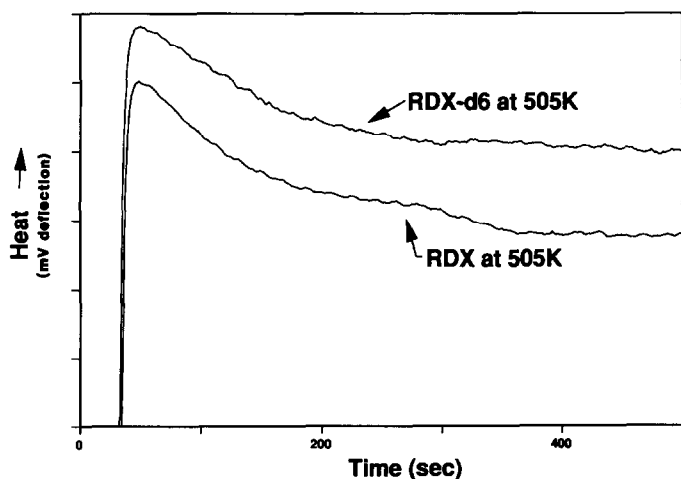


Fig. 4. IDSC thermochemical decomposition curves of RDX and RDX- d_6 (505 K).

constants in Table 1. All KDIE values in the 500–515 K temperature range represent a 1° KDIE for the thermochemical decomposition of liquid RDX and provide an averaged 1.64 KDIE value.

QUVA thermochemical decomposition analysis

Previously, a qualitative high pressure liquid chromatography (HPLC) analysis of HMX samples taken from quenched IDSC decomposition runs showed a progressive increase in UV-sensitive product formation along the

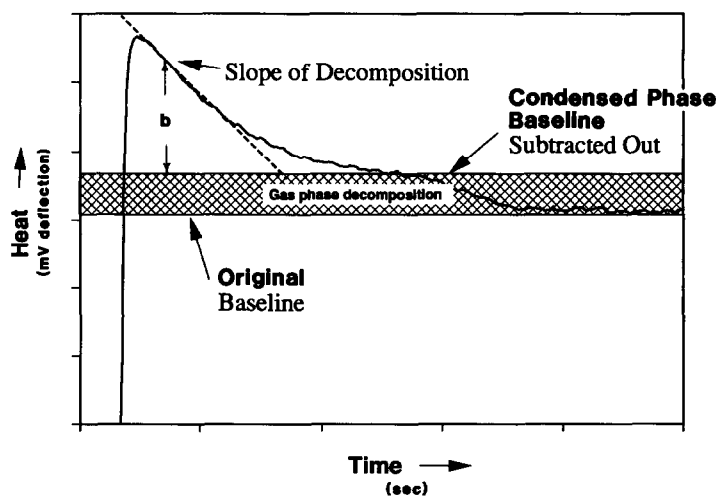


Fig. 5. Method of converting IDSC thermochemical decomposition curve to RDX (505 K) pseudo-first order kinetics plot.

IDSC decomposition curve, which emanated from the original HMX compound [8]. This HPLC analysis ensured that rate differences between the HMX and HMX- d_8 compounds result from the chemical reactions occurring during the decomposition process and not from differences in physical properties or characteristics. In order to quantitatively confirm that the KDIE values determined from heat evolution rates in IDSC analysis actually result from the kinetically controlled chemical reaction differences between the normal and deuterium labeled compound, and not from inherent differences in physical properties or extraneous thermophysical effects, the direct QUVA study was conducted. The QUVA results with liquid RDX and RDX- d_6 then were compared with our IDSC results. The QUVA study was accomplished at constant temperature (485 K), 7 K above the RDX melting point (477 K), and the decreasing concentration of RDX or RDX- d_6 at various time intervals could be directly determined from the chemical reactions producing RDX's lower molecular weight gaseous products throughout the decomposition process. A lack of large amounts of undecomposed RDX condensate at the test tube walls above the dark residue in the test tube bottom, and a lack of residue on the underside of the aluminum capping the test tube suggests that sublimation was not a critical factor in the depletion of RDX or RDX- d_6 samples. The RDX or RDX- d_6 concentration remaining at various stages of the decomposition was determined by UV absorption, and the percentage of residual RDX or RDX- d_6 was plotted as its natural logarithm against its corresponding quenched decomposition time. A linear pseudo-first order plot (Fig. 6) is found for both RDX and RDX- d_6 with a creditable regression rate correlation of 0.96 and 0.97 respectively, where the slope equals the rate constant for each com-

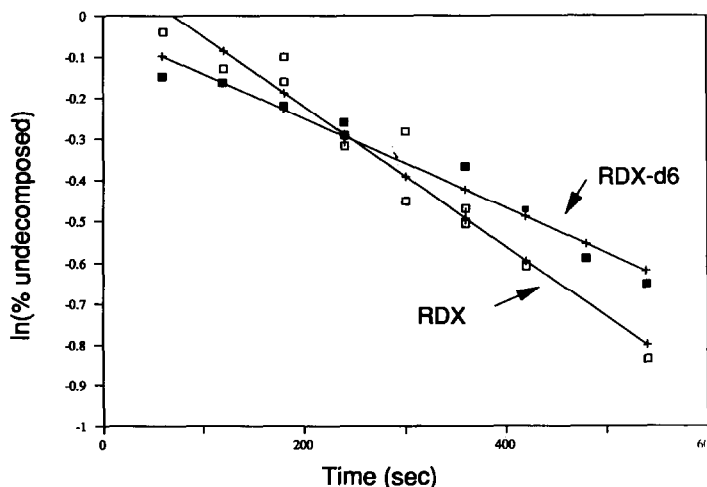


Fig. 6. QUVA pseudo-first order kinetics plot of RDX and RDX- d_6 (485 K) decompositions.

pound: $k_h(\text{RDX}) = -0.001702 \text{ s}^{-1}$ and $k_d(\text{RDX-}d_6) = -0.001087 \text{ s}^{-1}$. The k_h/k_d ratio reveals a 1° KDIE equal to 1.57 for the liquid RDX thermochemical decomposition process.

DISCUSSION

A KDIE is observed when deuterium atom substitution for the hydrogen nuclei of a chemical compound causes a rate change during a chemical reaction or process. This rate change occurs only when the deuterium labeled site in the compound's chemical structure or a position in the near vicinity of this labeled site participates in the slowest chemical reaction, and in doing so, selectively reveals the rate-controlling mechanistic step amid numerous sequential and parallel reactions driving the thermochemical decomposition process. This rate-controlling step generally involves the dissociation or rupture of a specific covalent bond and is perhaps the most important mechanistic feature taking place during the thermochemical decomposition's pathway, because it ultimately determines the overall rate at which a thermochemical decomposition process proceeds and kinetically regulates its rate of energy release. Identification of this rate-controlling step may be obtained using rate constant ratios of the unlabeled and analogous deuterium substituted compound, or can be determined more indirectly using other parametric ratios related to reaction rates such as induction times [3,8], critical temperatures [5,6,8], burning rates [6,7,10–12] and shock initiation velocities [9,13]. Since the first use of the condensed phase KDIE approach with an energetic compound, 2,4,6-trinitrotoluene (TNT), and its deuterium labeled analogue (TNT- α - d_3) by IDSC analysis [3], the rate-controlling mechanistic step has also been determined for the thermochemical decomposition processes of 2,2',4,4',6,6'-hexanitrobibenzyl (HNBB) [4], 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [5], HMX [8] and RDX [7] via the IDSC analysis method, and for RDX and HMX using the TGA analysis method [9]. Extension of the KDIE approach with these energetic compounds into the faster pyrolytic deflagration process [6,8] and into the more drastic higher temperature, pressure or rate combustion [6,7,10–12] thermal explosion [5,8] and detonation regimes [9,13], reveals two important points. Firstly, it demonstrates that a significant degree of kinetic control participates in these higher energy phenomena; secondly, it reveals that the same rate-controlling mechanistic step is present in these higher order regimes as that observed by IDSC and TGA during atmospheric pressure thermochemical decomposition investigations. A definite mechanistic relationship between the thermochemical decomposition process of an energetic compound and these higher energy phenomena apparently exists [21–24] and further suggests that the thermochemical decomposition process may be an integral part of them [12,23,24].

TABLE 2

Comparative KDIE values in liquid RDX decomposition

Method of analysis	Temp. range (K)	KDIE	Ref.
IDSC	500–515	1.64	This work
QUVA	485	1.57	This work
TGA	479–489	1.56	9

The IDSC technique measures the RDX and RDX- d_6 chemical depletion kinetics by following heat evolution rates. These rates are considered as being proportional to the global rate at which various exothermic chemical reactions convert the original compound to product species [14]. The validity of this proportionality is demonstrated by direct UV absorption analyses (QUVA) of isothermally decomposed liquid RDX samples quenched at various times along the decomposition process pathway. Direct QUVA analysis of the decreasing RDX compound concentration confirms that the IDSC heat evolution rates result from these exothermic chemical reactions producing the decomposition. Comparing the RDX and RDX- d_6 QUVA determined depletion rates at 485 K, the 1° KDIE is also observed. The value of 1.57 matches closely the averaged KDIE value of 1.64 of the IDSC analysis (Table 2) determined in the 500–515 K temperature range. While a previous IDSC investigation of the HMX/HMX- d_8 decomposition process qualitatively showed that KDIE values result from chemical reactions and not from extraneous thermophysical phenomena or physical property differences [8], this QUVA and IDSC analysis comparison offers quantitative confirmation for this direct proportionality [14]. It should be noted, however, that this correlation holds true throughout the entire process only when an energetic compound produces mainly gaseous products without the significant formation of condensed phase products. In cases where the energetic compound decomposes mainly to condensed phase products (e.g., TNT [3]), one must be careful to ensure that the portion of the IDSC decomposition curve being analyzed is representative of the original compound's thermochemical decomposition behavior and not that of the subsequent condensed phase product intermediates generated from the original energetic compound itself [3,8]. A vivid comparison of the isothermal IDSC- and QUVA-based KDIE results with those obtained in a similar temperature region by a previous isothermal thermal gravimetric analysis (TGA) study [9] is shown in Table 2; again, there is close agreement among the 1° KDIE values obtained by all three thermal analysis methods, TGA (1.56), IDSC (1.64) and QUVA (1.57), even though they each use a different analytical principle (TGA (weight loss), IDSC (heat evolution), and QUVA (spectroscopic UV absorption)) to monitor an energetic compound's global decomposition rate.

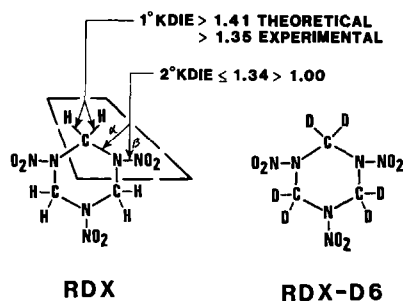


Fig. 7. Possible kinetic deuterium isotope effects in the RDX and RDX- d_6 chemical structure.

The IDSC thermochemical decomposition study of neat, liquid RDX and RDX- d_6 displays a 1° KDIE (1.64) in the 500–515 K temperature range and verifies covalent carbon–hydrogen bond dissociation [7,9] as being its probable rate-controlling mechanistic step *. All KDIE values in Table 1 fall above the theoretical 1.41 high temperature minimum value [26] and the experimental 1.35 value [27,28] for a 1° KDIE. Assignment of this 1° KDIE value is further supported by their mathematically normalized value at standard temperature conditions using a simple 1° KDIE model [29]. These standard temperature KDIE results (ave. = 3.55) also far exceed the 1° KDIE value of 2.5 suggested as being a reasonable minimum threshold at 298 K [30]. The molecular structure of RDX comprises three repeating methylene nitramine fragments bonded together in a cyclic head-to-tail arrangement making the six methylene hydrogen atoms, or six substituted deuterium atoms in RDX- d_6 , chemically equivalent during a decomposition process (Fig.7). Dissociation of any C–H bond in RDX or C–D bond in RDX- d_6 or condensed phase fragments derived from them would produce a

* In certain cases with solvolyzed chemical reactions a KDIE may result without C–H bond rupture occurring in the slowest step of a given chemical reaction. Such cases can exist, (a) when the reaction contains a C–H bond dissociation/reformation equilibrium step just prior to its slower rate-determining step [25a], or (b) sometimes when the solvent itself participates in the reaction's subsequent rate-determining step immediately after C–H bond rupture occurs as specifically illustrated in a three step solvated H/D exchange reaction [25b]. In the absence of any current experimental verification that such selected cases participate during the thermochemical decomposition process of RDX or any other energetic compound, and in view of past energetic compound KDIE mechanistic and product formation studies [24], covalent C–H bond rupture is assigned as the probable rate-controlling mechanistic step. One cannot totally discount the possibility that such a specific case might be masked from detection by the thermochemical decomposition's very complex nature in both the solid state or liquid phase but, from a broad perspective of the overall decomposition process, substitution of deuterium atoms for hydrogen has a regulating effect on the global rate at which the liquid RDX thermochemical decomposition proceeds; therefore covalent C–H bond dissociation is an obvious rate-controlling mechanistic feature which is a strong indication that it also constitutes the rate-controlling step for this complex process.

1° KDIE when this specific bond rupture occurs during the slowest chemical reaction comprising the thermochemical decomposition process. Either C–N bond scission in the α -position, or N–NO₂ bond dissociation in the β position relative to the labeled C–H/C–D bond could produce a 2° KDIE, while other factors could possibly even produce an inverse KDIE [8]. The 1° KDIE values in Table 1 identify covalent C–H bond dissociation as the rate-controlling mechanistic feature which kinetically regulates the global thermochemical decomposition rate of liquid RDX. This rate-controlling bond dissociation does not necessarily represent the first or initial bond rupture and occurs at some point along the mechanistic sequence of chemical reactions which drive the decomposition process. This key C–H dissociation must come from either the original RDX molecule, or from a molecular fragment which is present in the condensed liquid phase; otherwise, given the nature of this IDSC experiment itself where the contribution from the gaseous decomposition of gaseous species is subtracted out (Fig. 5), no rate constant difference between RDX and RDX-*d*₆ would be detected in the IDSC decomposition curve.

Liquid RDX's condensed phase KDIE behavior and that of its higher cyclic nitramine homologue, HMX, are strikingly different in spite of their similar molecular structures. Discounting conformational dissimilarities between six- and eight-membered nitramine ring systems which could have some significance in a high temperature liquid phase decomposition process, the molecular structures of RDX and HMX initially differ only by the number of repeating methylene nitramine structural units (Fig. 8). RDX comprises three such units forming a six-membered ring, while HMX forms an eight-membered ring with four –CH₂–NNO₂ structural units; yet, both kinetic and mechanistic differences are displayed by the decomposition processes of liquid RDX and HMX which could proceed by a unimolecular [8], bimolecular [8], or perhaps an even more complex pathway. Liquid RDX follows pseudo-first order kinetic behavior while liquid HMX apparently follows a more complex autocatalytic kinetic function when plotted as part of an entire decomposition curve where HMX passes through three con-

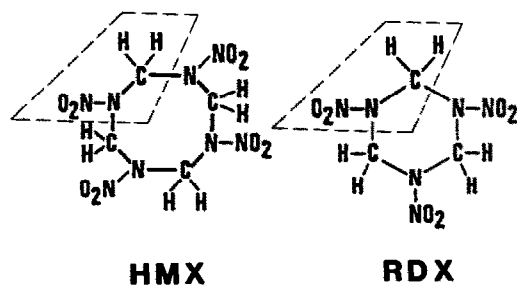


Fig. 8. Chemical structure comparison of the HMX and RDX molecules.

densed phases [8]. The RDX pseudo-first order kinetic behavior is seen in both the IDSC (Fig. 2) and QUVA (Fig. 6) kinetic plots; and in the case of the IDSC decomposition curve, the decay portion always provided a better empirical fit to the first order kinetic plot than to the autocatalytic equation previously used for evaluating HMX [8]. When IDSC analyses were conducted several degrees below the HMX melting point, the resultant δ -HMX polymorph passed through three condensed phase physical states (solid, mixed-melt, liquid) during the same sample run, and in doing so, produced a decomposition curve following an autocatalytic kinetics function [6,8,10,11, 24]. The latter decay portion of IDSC decomposition curve corresponds to the HMX liquid phase which is evaluated using a dx/dt versus $x(1-x)$ autocatalytic kinetic function where x equals the mole fraction of decomposed HMX at specific decomposition time intervals and dx/dt is equal to the height (b) of the decomposition curve above the baseline at a given time divided by the curve's total area [24,31]. Similar kinetic behavioral differences recently have been observed in high pressure (GPa) diamond anvil decomposition studies of liquid RDX (in which all indications are that RDX decomposition occurs in the liquid phase) [32] and the solid β -HMX polymorph [33]. As with the ambient pressure IDSC decomposition studies on liquid RDX, plus δ -HMX and its nonpolymorphic liquid state, the high pressure diamond anvil decomposition studies reveal that liquid RDX follows first order kinetics, while solid β -HMX proceeds along an autocatalytic pathway. The condensed phase KDIE approach reveals one further difference between the liquid RDX [7,9] and HMX thermochemical decomposition processes [8,9]. The liquid RDX's 1° KDIE identifies covalent C-H bond dissociation as the rate-controlling mechanistic step which kinetically regulates its thermochemical decomposition's global energy release rate; in contrast, the rate-controlling mechanistic step for the liquid HMX decomposition process results from an apparent C-N bond dissociation as displayed by a 2° KDIE [8]. This mechanistic difference between RDX and HMX decomposition appears only in the liquid state (Table 3); solid state HMX decomposition analyzed in a temperature range corresponding to its

TABLE 3
Comparative KDIE data on RDX and HMX decomposition

Compound	Physical state	KDIE ^a	Method of analysis	Ref.
RDX	Liquid	1°	TGA	9
		1°	QUVA	This work
		1°	IDSC	This work
HMX	Liquid	2°	IDSC	8
HMX	Solid	1°	IDSC	8
RDX	Solid	1°	TGA	9
		1°	TGA	9

^a 1°, Primary; 2°, secondary.

δ -polymorph by both IDSC [8] and TGA [9], provides a 1° KDIE as does solid state RDX decomposition analyzed by TGA [9]. These results indicate that unlike HMX, covalent C–H bond rupture constitutes the same rate-controlling mechanistic step for both the solid and liquid RDX decomposition process. Interestingly, both HMX/HMX- d_8 and RDX/RDX- d_6 sample sets display the same rate-controlling covalent C–H bond dissociation (1° KDIE) during high pressure (3.6 and 7.0 MPa) combustion [6,7,12,23], demonstrating for the first time that this same mechanistic feature plays a significant role in kinetically determining the burning rate of both cyclic nitramines [12,23,24].

CONCLUSIONS

The similar condensed phase primary kinetic deuterium isotope effect (1° KDIE) displayed by both isothermal differential scanning calorimetry (IDSC) analysis and by direct UV absorption on sequentially quenched RDX and RDX- d_6 samples (QUVA) experimentally confirms that the IDSC heat evolution rate is proportional to the global decomposition rate at which an energetic compound is converted to final products by a myriad of complex kinetically controlled chemical reactions. While these IDSC and QUVA analyses, plus a previously reported isothermal TGA study, rely on dissimilar heat evolution, spectroscopic UV absorption, and weight loss analytical principles respectively, they all display a 1° KDIE of similar magnitude. This comparative KDIE result demonstrates that the condensed phase KDIE emanates from chemical reaction rate differences involving a mechanistic rate-controlling covalent C–H or C–D bond dissociation and not from a dissimilarity in physical properties or extraneous thermophysical effects between the normal and deuterium labeled nitramine heterocycles. The kinetic and mechanistic thermochemical decomposition behavior of liquid RDX contrasts with that displayed by its eight-membered octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) homologue. While cyclic six-membered liquid RDX provides an empirical pseudo-first order kinetic plot and is kinetically controlled in its energy release rate by a mechanistic pathway involving covalent C–H bond dissociation (1° KDIE), liquid HMX displays an autocatalytic kinetic behavior and a C–N bond dissociation (2° KDIE) as its rate-controlling mechanistic step. The C–H bond rupture observed in the thermochemical decomposition processes of both liquid and solid RDX, plus solid state HMX, also appears to be the same rate-controlling mechanistic feature which kinetically determines the global RDX and HMX burning rate during high pressure (3.6 and 7.0 MPa) combustion.

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