a saturated methanolic solution of ammonia (30 mL) and the reaction mixture was left to stand at room temperature for 20 h. The separated product was filtered off, the filtrate was evaporated to dryness and treated with water (5 mL), and the residue was filtered. The combined products were crystallized from ethanol: mp 247–248.5 °C (yield 53.5 mg, 30%); MS *m/e* 211 (M); ^{1}H NMR (Me_2SO-d_6) δ 7.26 (d, H_5), 7.74 (d, H_6), 8.0–7.4 (m, Ph), 3.33 (s, NH_2), $J_{5,6} = 4.5$ Hz.

Anal. Calcd for $C_{11}H_9N_5$: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.77; H, 4.55; N, 33.36.

(B) Compound **19** ($R = Ph$, $R_1 = OMe$) (50 mg) was added to a saturated methanolic solution of ammonia (10 mL) and the reaction mixture was heated in an autoclave at 100 °C for 5 h. Upon evaporation of the solvent, the residue was crystallized from ethanol. The compound was found to be identical in all respects with product obtained as described under A.

Acknowledgment. We thank the Boris Kidrič Fund for partial support of the research.

Registry No.—**1**, 274-79-3; **2**, 63744-21-8; **3**, 57948-41-1; **4**, 24241-18-7; **5**, 63744-22-9; **5** HBr, 63744-23-0; **6**, 63744-24-1; **7**, 63744-25-2; **8** HBr, 63744-26-3; **9**, 63744-27-4; **10**, 63744-28-5; **11**, 274-82-8; **12**, 63744-29-6; **15**, 63744-30-9; **16**, 63744-31-0; **17** ($R = R_1 = H$), 63286-29-3; **17** ($RR_1 = PhCH{=}$), 63744-32-1; **17** ($RR_1 = {=}CHNMe_2$), 63744-33-2; **18** ($R = H$, $X = Cl$), 63744-34-3; **18** ($R = Ph$, $X = Cl$), 63744-35-4; **19** ($R = Ph$, $R_1 = OMe$), 63744-36-5; **19** ($R = Ph$, $R_1 = OEt$), 63744-37-6; **19** ($R = Ph$, $R_1 = NH_2$), 63744-38-7; **20** ($R = H$, $R_1 = SPh$), 63744-39-8; **20** ($R = Ph$, $R_1 = SPh$), 63744-40-1; 5-chloroimidazo[1,2-*a*]pyrazine, 63744-41-2; 2-amino-6-chloropyrazine, 33332-28-4; 2,6-dichloropyrazine, 4774-14-5; 2-*N,N*-dimethylaminomethylenehydrazinopyrazine, 63744-42-3; sodium thiophenolate, 930-69-8; ammonia, 7664-41-7; *N,N*-dimethylformamide dimethyl acetal, 4637-24-5; hydrazinopyrazine, 54608-52-5.

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Deuterium Isotope Effects in the Thermochemical Decomposition of Liquid 2,4,6-Trinitrotoluene: Application to Mechanistic Studies Using Isothermal Differential Scanning Calorimetry Analysis

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The thermochemical decomposition of liquid 2,4,6-trinitrotoluene (TNT) produces a primary kinetic deuterium isotope effect when its methyl moiety is deuterium labeled. The novel integration of the deuterium isotope effect with isothermal differential scanning calorimetry analysis provides the first directly measured mechanistic evidence that carbon–hydrogen bond rupture in the TNT methyl group constitutes the rate-determining step of the thermochemical decomposition reaction. This thermochemical reaction possesses an induction period during which a single species forms from TNT and catalyzes a sustained exothermic decomposition. An expression was derived that correlated deuterium/hydrogen induction time ratios with inaccessible hydrogen/deuterium rate constant ratios during this induction period. Direct induction time measurement allowed deuterium isotope effect evaluation before interfering side reactions diluted the magnitude of the isotope effect during the latter stages of exothermic decomposition. Hydrogen donor effects suggest that the rate-determining carbon–hydrogen bond rupture proceeds homolytically. A large negative entropy of activation reveals a high degree of orderliness during the decomposition.

The kinetic deuterium isotope effect has proved to be a powerful tool in mechanistic elucidations of gaseous and solvolyzed chemical reactions. Recently, isothermal differential scanning calorimetry (isothermal DSC) proved its value as a rapid and elegant technique for determining kinetic parameters (e.g., reaction rate, rate constant, reaction order, activation energy) in thermochemical decomposition reactions of liquified nitrated organic compounds.[2-4] Because liquid organic compounds constitute a homogeneous phase, and because an isothermal DSC curve is directly proportional to a reaction rate that is easily converted into a rate constant, we felt the deuterium isotope effect concept could be integrated

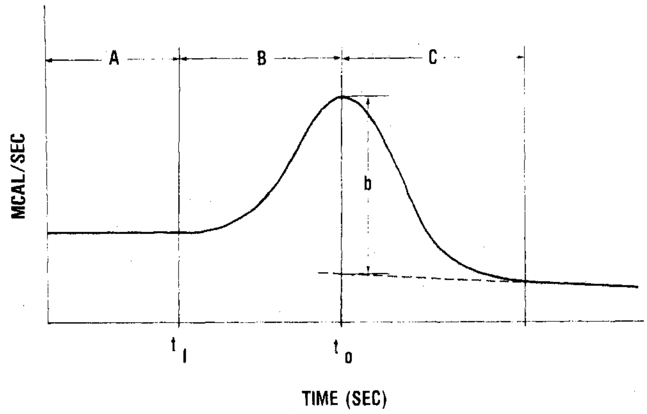
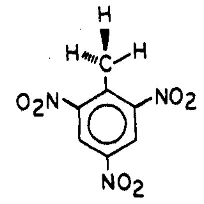


Figure 1. Generalized isothermal DSC trace for TNT comprised of an induction period (A), exothermic acceleratory phase (B), and decay phase (C). Note that mcal/s is directly proportional to reaction rate.[2]

with isothermal DSC analysis to provide novel mechanistic information previously unobtainable in thermochemical decomposition studies.

This paper describes the integration of deuterium isotope effect studies with the isothermal DSC analysis technique to elucidate the rate-determining step in the thermochemical decomposition reaction of liquid 2,4,6-trinitrotoluene (TNT).



This study represents the first direct mechanistic conformation that carbon–hydrogen bond rupture in the benzylic methyl moiety is the rate-determining step that initiates the exothermic decomposition of liquid TNT.

Results and Discussion

Isothermal DSC is an excellent method to conveniently determine the kinetic parameters in the thermochemical decomposition reaction of liquid polynitro organic compounds. Direct kinetic data is rapidly obtained that allows the determination of reaction rates (r), rate constants (k), reaction orders (n), preexponential factors (Z), and activation energies (E_a).[2,3] Secondly, isothermal DSC analyzes thermochemical decomposition reactions in a homogeneous liquid phase where crystal-lattice stabilization effects are not a complicating factor and where the process is likely to be first order.[2,5] The direct measurement of pure molten solutions also negates the presence of potential solvent[6] and/or dilution effects that could interfere with the true mode of bulk thermochemical decomposition. Finally, liquid 2,4,6-trinitrophenyl compounds generate only small amounts of gaseous products during thermochemical decomposition and convert instead mainly to molecular, self-condensing derivatives.[7–9] Thus, isothermal DSC provides an attractive alternative to gas-evolution techniques which often produce conflicting kinetic results in low gas-evolving compounds like 2,4,6-trinitrotoluene (TNT).[9,10]

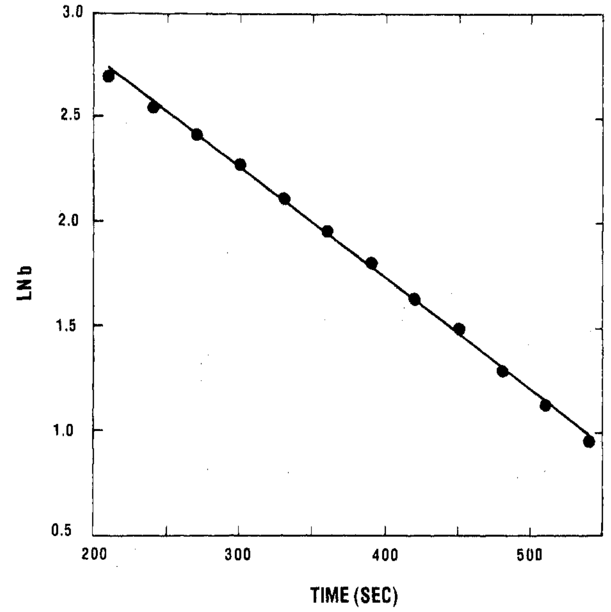


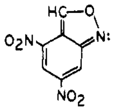
Figure 2. First-order rate constant graph for TNT-d_3 at 263 °C.

Table I. Decay Phase Rate Constants (s^{-1})

Temp, °C	TNT	TNT-d_3
245	3.38×10^{-3} [b]	2.18×10^{-3} [a]
251	4.09×10^{-3} [c]	3.46×10^{-3} [a]
257	5.92×10^{-3} [b]	4.32×10^{-3} [a]
263	8.36×10^{-3} [b]	5.61×10^{-3} [b]
269	11.4×10^{-3} [a]	8.58×10^{-3} [a]

[a] Average value for three runs. [b] Average value for four runs. [c] Average value for five runs.

Polynitro aromatic compounds possessing benzylic hydrogen atoms adjacent to an o-nitro group show a higher sensitivity toward thermochemical decomposition than other structural isomers. An oxidation–reduction mechanism that involves chemical interaction between the benzylic substituent and the neighboring o-nitro group is one reason postulated to explain this thermally reactive behavior.[8,9,11–13] Past analyses of thermochemically decomposed TNT at temperatures ranging between 195 and 330 °C revealed the following products which necessitate rupture of the methyl carbon–hydrogen bond at some point during the decomposition reaction:[8,9] 4,6-dinitroanthranil (**1**), 2,4,6-trinitrobenzyl alcohol (**2**), 2,4,6-triintrobenzaldehyde (**3**), 2,4,6-trinitrobenzoic acid (**4**), and 1,3,5-trinitrobenzene (**5**). Recently, isothermal DSC analysis was employed to follow liquid TNT's thermochemical decomposition reaction within a 245–269 °C range. The study was conducted at 6 °C increments, and kinetic parameters, including the rate constant, were determined.[10] The homogeneous nature of the liquid TNT, the ability to conveniently determine rate-constant data by isothermal DSC, plus the thermochemical decomposition product analyses that revealed carbon-hydrogen bond rupture occurring in TNT's methyl moiety[8,9] represented all the conditions necessary to allow the study of potential kinetic deuterium isotope effects during TNT's thermochemical decomposition reaction. Detection of a deuterium isotope effect from rate-constant ratios (k_H/k_D) between TNT and its α,α,α-trideuterio analogue (TNT-d_3) would confirm the potential importance of the carbon–hydrogen bond rupture in this thermochemical decomposition mechanism.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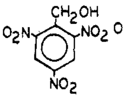
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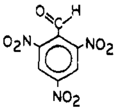
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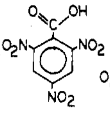
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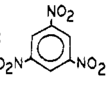
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Decay Phase Analysis. Isothermal DSC analysis of liquid TNT (mp 81–82 °C) was taken at 6 °C increments from 245

Table II. Decay Phase Kinetic Data

Compd	n (order)	E_a, kcal mol^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu	k_H/k_D
TNT	0.97 ± 0.07	29.4 ± 1.4	28.35 ± 0.01	−16.4 ± 0.1	1.35 ± 0.02[a]
TNT-d_3	0.86 ± 0.06	29.9 ± 1.6	28.85 ± 0.01	−16.1 ± 0.1	

[a] Average deuterium isotope effect for all five temperatures (Table I).

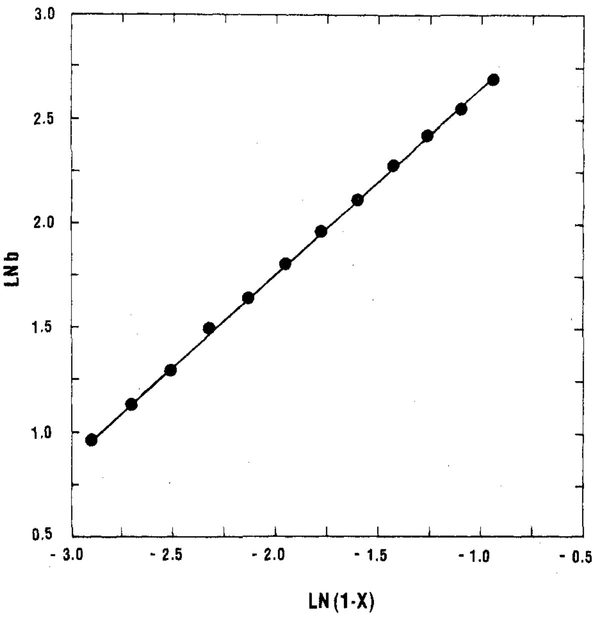


Figure 3. Order plot (slope = 0.89) for TNT-d_3 at 263 °C. Analogous TNT order plot (slope = 1.01).

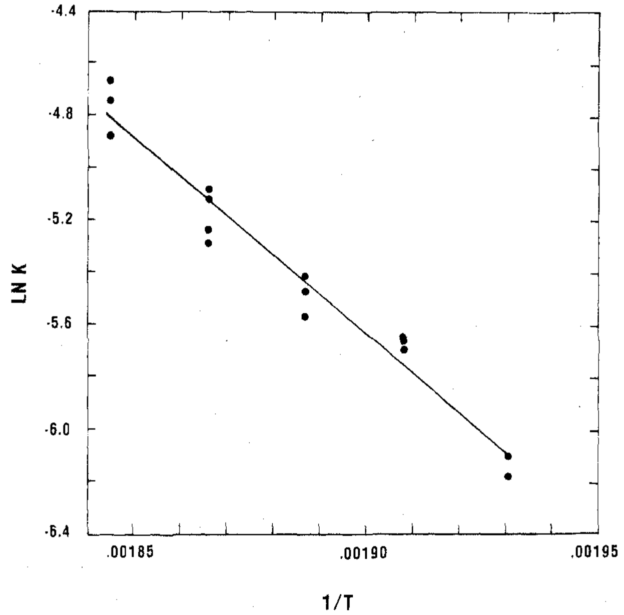


Figure 4. Decay phase Arrhenius plot for activation energy (E_a) of TNT-d_3.

to 269 °C. A slightly skewed bell-shaped curve was produced. This curve was comprised of an induction period A, an exothermic acceleratory phase B, and a decay phase C, where the decomposition reaction dissipates to completion (Figure 1). During the decay phase C, the deflection of the isothermal DSC curve (b) is measured as the difference between the curve and baseline at specific time intervals. Simpson's rule is then employed to integrate these closely spaced deflection measurements to easily obtain the desired kinetic parameters previously discussed.[2,3,10] Kinetic parameters obtained in the isothermal DSC analysis of TNT and TNT-d_3 from the decay phase are illustrated in Tables I and II. Figure 2 is a first-order plot of ln b vs. time for TNT-d_3 at 263 °C, from which the rate constant k was obtained as the slope ($-k$). Figure 3 illustrates the order plot obtained for this compound, and Figure 4, in which ln k is graphed against reciprocal temperature, provides the activation energy cited in Table II for TNT-d_3 (see paragraph at the end of paper about supplementary material). The change in enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) in this thermochemical decomposition reaction was readily calculated (eq 1 and 2) from the rate constant (k) and activation energy (E_a) values obtained in the isothermal DSC analysis at the temperatures listed in Tables I and II.

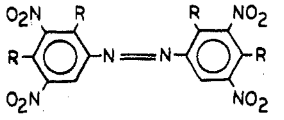
$$\Delta H^* = E_a - RT \tag{1}$$

$$\Delta S^* = 2.303R\left(\log k - \log\left(\frac{k}{h}\right) - \log T\right) + \frac{\Delta H^*}{T} \tag{2}$$

The magnitude and sign of ΔS^* reflects a very high degree of orderliness once the self-sustained, exothermic decomposition is initiated and could suggest a cyclic structural interaction.[14] A cyclic interaction reasonably could result in a transition-state species formed by an intramolecular reaction between the o-nitro group and methyl moiety of TNT.[7,8,11-13]

A significant deuterium isotope effect is found for TNT (Table II). Carbon–hydrogen bond rupture in the methyl moiety during the rate-determining step would produce a deuterium isotope effect ratio equal to or greater than 1.41.[15] However, the magnitude of the observed isotope effect during the decay phase (Table II) of TNT's thermochemical decomposition reaction is not definitive for a primary isotope effect. This 1.35 value is slightly lower than most ratios cited. However, TNT's inherent chemical structure ruled out a secondary isotope effect and suggested the low 1.35 value to be a dilution of the primary isotope process.

The isothermal DSC technique measures the total reaction rate during the decay phase C. Competing side reactions can produce decomposition products in which no carbon–hydrogen rupture occurs.[9] These reactions would have different rate-determining steps that contribute to the total reaction-rate measurement revealed by isothermal DSC during the decay phase. These competing side reactions, not involving carbon–hydrogen bond rupture, would dilute the magnitude of the actual deuterium isotope effect, since they comprise a portion of the total reaction-rate measurement. Previous product isolation of dimeric TNT reduction products that contained azo-6 and/or azoxy-7 linkages with undisturbed methyl groups strongly suggests this to be the case.[9] Analysis of the induction period A of the isothermal DSC curve offered an answer to this dilemma.



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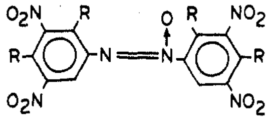

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R= H, CH_3

Induction Period Analysis. High-pressure liquid chromatographic analysis was performed on TNT samples that were thermochemically decomposed only during the induction period A. Analysis revealed an apparent single, unidentified

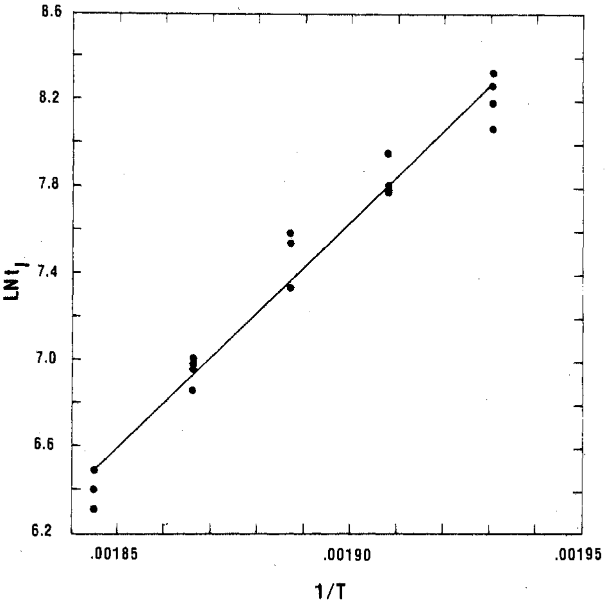

Figure 5. Induction period Arrhenius plot for activation energy ($E_a{}^I$) of TNT-d_3.

compound I formed from TNT during the induction period A and prior to the thermochemical decomposition reaching its exothermic acceleratory phase B. A trace amount of compound I was isolated and was added to a pure TNT sample. Isothermal DSC analyses of this sample (263 °C) showed a significant rate enhancement; the induction period was decreased by a factor of nearly 2.5. Thus, compound I appears responsible for catalyzing the thermochemical decomposition of *TNT* during the induction period. If the apparent catalytic precursor species I forms from TNT by carbon–hydrogen bond rupture in the methyl moiety, a pure, undiluted deuterium isotope effect could be operating during the induction period A. The problem of obtaining data that defined this potential deuterium isotope effect was addressed next.

Evaluation of the k_H and k_D rate constants during the thermochemical decomposition's decay phase C depends upon the isothermal DSC curve's deflection from the baseline *b*. The horizontal induction period A generates no such deflection; however, the induction time (t_I) can be used to obtain deuterium isotope effects and is conveniently measured from the isothermal DSC curve.

The induction time (t_I) of a catalytic decomposition curve is defined as the time elapsed from sample pan placement into the DSC instrument until the initial deflection of the exothermic acceleratory phase B from the horizontal baseline comprising the induction period A (Figure 1). The t_I value for TNT has been used to calculate the induction period reaction's activation energy ($E_a{}^I$) for compound I formation.[10] Two mathematical approximations were invoked to arrive at eq 3 where k is the decomposition reaction's rate constant and i_I the small mole fraction of compound I formed at a given induction time, t_I.

$$k = i_I/t_I \tag{3}$$

Equation 4 was obtained by taking the natural logarithm of the Arrhenius equation. Equation 5 resulted by setting eq 4 equal to eq 3 in logarithmic form.

$$\ln k = E_a{}^I/RT + \ln Z \tag{4}$$

$$\ln k = \ln i_I - \ln t_I = E_a{}^I/RT + \ln Z \tag{5}$$

A graphical plot of ln t_I vs. the reciprocal temperature ($1/T$) afforded a slope that when multiplied by the ideal gas constant produced $E_a{}^I$.[10] Figure 5 displays the graphical data obtained for TNT-d_3. Equation 5 serves as the starting point for determining deuterium isotope effects using t_I data.

Table III. Induction Period Kinetic Parameters

Compd	E_a, kcal mol^{-1}	t_{ID}/t_{IH}
TNT	46.5 ± 1.5	1.66 ± 0.2
TNT-d_3	41.6 ± 1.8	

Equation 5 may be rearranged to yield eq 6.

$$\ln i_I = \ln k + \ln t_I \tag{6}$$

Assuming the mole fraction (i_I) of compound I, generated during the induction period, must reach a specific threshold concentration to catalyze TNT's thermochemical decomposition into the acceleratory phase B,[16] only t_I and k may vary between the deuterated and nondeuterated TNT reactions. Assuming i_I to be a constant threshold concentration, the following equations are derived:

$$\ln k_H + \ln t_{IH} = \ln i_I = \ln k_D + \ln t_{ID} \tag{7}$$

$$\ln k_H + \ln t_{IH} = \ln k_D + \ln t_{ID} \tag{8}$$

and finally

$$\frac{k_H}{k_D} = \frac{t_{ID}}{t_{IH}} \tag{9}$$

Equation 9 establishes the necessary relationship between nondeuterated/deuterated rate constants and deuterated/nondeuterated induction times to determine deuterium isotope effects that operate during thermochemical decomposition induction periods. Direct measurement of t_I values from isothermal DSC curves for deuterated and nondeuterated liquid-phase TNT allows deuterium isotope effects to be evaluated by t_{ID}/t_{IH}, where t_{ID} represents the deuterated compound's induction time and t_{IH} the nondeuterated analogue. Results showing the t_{ID}/t_{IH} values obtained are given in Table III, as is $E_a{}^I$ for each compound.

A primary deuterium isotope effect is revealed during the thermochemical decomposition reaction's induction period A. The 1.66 value clearly represents a primary kinetic isotope effect.[17] The minimum value expected for the primary hydrogen/deuterium isotope effect would equal 1.41. This minimum value could be expected when a high-temperature limit is reached where the isotope effect depends solely upon the vibrational frequencies of each bond.[15] Indeed, if the primary deuterium isotope effect for molten TNT was normalized from the very high 245–269 °C temperature range into the 25–100 °C range generally employed for deuterium isotope effect studies in solvolyzed reactions, the 1.66 value of TNT would be more profound. This data (Table III) represents the first direct experimental verification that benzylic carbon–hydrogen bond rupture is the critical rate-determining step in the thermochemical degradation of liquid TNT. Apparently, this rate-determining carbon–hydrogen bond rupture results in the accumulation of a threshold concentration of compound I which then catalytically initiates the self-sustained, exothermic thermochemical reaction. The deuterium isotope effect data obtained from the induction period provides a clearer picture of the initiation mechanism before other interferring side reactions dilute kinetic data and complicate mechanistic elucidation.

Hydrogen Donor Effects. Hydroquinone (HQ) is an effective scavenger for reactions that proceed by a radical mechanism. One then might expect hydroquinone to rapidly react with the products obtained from TNT's benzylic carbon–hydrogen bond rupture if radical species are produced. When a 3.7 mol % HQ/TNT mixture was thermochemically decomposed by isothermal DSC at 263 °C, molten TNT's decomposition reaction greatly accelerated.[18] The decomposition reaction accelerates so markedly that the induction period A totally disappears. With pure TNT samples, approximately 2 min were required for thermal equilibration to be achieved, and an induction period followed as part of the normal isothermal DSC curve (Figure 1). However, the 3.7% HQ/TNT samples displayed no induction period, and following the 2-min thermal equilibration a steep exothermic slope characterized the 3.7% HQ/TNT reaction as being well advanced into the self-sustained exothermic acceleration phase B. This rapid exothermic reaction suggests that any measurable induction period A in the 3.7% HQ/TNT reaction is considerably less than 2-min long and that a bimolecular reaction occurs between TNT and hydroquinone.

Formation of compound I during the induction period apparently is initiated from a hydrogen species being generated by the rate-determining carbon–hydrogen bond cleavage in pure TNT. Hydroquinone possesses a labile hydroxyl hydrogen which could be introduced to the TNT molecule more readily than by a methyl group's carbon–hydrogen bond rupture. Thus, very rapid catalysis of the molten TNT thermochemical decomposition reaction likely results from hydroquinone providing a more labile hydrogen species to a TNT molecule than can pure TNT in hydroquinone's absence. While hydroquinone is usually a hydrogen-atom donor, the possibility that it acted as a proton donor under our reaction conditions had to be addressed. To determine which type of hydrogen species was catalyzing TNT's molten thermochemical decomposition reaction, 3.7 mol % benzoic acid (BA), a proton donor, was mixed with TNT. Isothermal DSC analysis of the 3.7% BA/TNT samples (263 °C) produced a normal decomposition curve like that exhibited by pure TNT.[19] While the 3.7% BA/TNT[20] samples yielded an induction time only 8% less than that of pure TNT (Table IV), the relative acceleratory effect of hydroquinone is exceptionally dramatic. Assuming the 3.7% HQ/TNT thermochemical decomposition reaction possessed a maximum induction period A equal to the instrumental temperature equilibration time (ca. 120 s), hydroquinone represents a 60% reduction in pure TNT's induction period. Interestingly, hydroquinone accelerates the thermochemical decomposition of TNT mainly during the early induction period (60% a minimum value) as opposed to the exothermic acceleratory phase (45% a maximum value),[21] while benzoic acid shows its largest acceleration during the exothermic acceleratory phase (32%) vs. the induction period (8%).[21]

The tremendous induction period acceleration in the 3.7% HQ/TNT reactions leads to the conclusion that hydroquinone provides a hydrogen atom which rapidly catalyzes the thermochemical decomposition of liquid TNT. TNT's rapid decomposition in the presence of a hydrogen-atom donor strongly suggests that the rate-determining carbon–hydrogen bond rupture found to occur in pure TNT proceeds by a homolytic cleavage during the induction period.[22] This homolytic carbon–hydrogen bond rupture generates a chain-initiating hydrogen atom that leads to the production of compound I, which in turn must catalyze the exothermic decomposition reaction of TNT.

Conclusion

A deuterium isotope effect study was successfully integrated with isothermal DSC kinetic analysis to elucidate by direct experiment the rate-determining step in liquid TNT's thermochemical decomposition reaction. This application of the deuterium isotope effect to isothermal DSC analysis provided mechanistic information, heretofore unobtainable, which is important in elucidating thermochemical reaction pathways of compounds in a homogeneous liquid phase. Crystal lattice stabilization effects and the influences of solvent or dilution were eliminated as factors that complicate the kinetic evaluation of thermochemical reactions. A primary deuterium isotope effect was obtained that directly revealed the critical bond rupture responsible for initiating TNT's sustained exothermic decomposition reaction.

A significant deuterium isotope effect (1.35) was observed during the decay phase C (Figure 1) of TNT's thermochemical decomposition reaction where sustained exothermic degradation occurs. But, competing, simultaneous reactions proceed during this latter decay phase C and dilute the observed k_H/k_D isotope ratio. The decay phase C represents a total reaction rate and includes the reaction rates of compounds that form from TNT without carbon–hydrogen bond rupture occurring in the methyl moiety. The previous isolation of **6**- and **7**-type compounds from TNT thermochemical decomposition reactions supports this.[8,9] This work has shown that induction time ratios, obtained directly from isothermal DSC curves, can be used in lieu of undeterminable rate-constant ratios to determine the deuterium isotope effect during the initial induction period A. High-pressure liquid-chromatography studies at this laboratory revealed a singular catalytic species, compound I, formed from TNT during the induction period; thus, reactions found in the decay phase C that dilute the isotope effect are likely absent in the induction period A. Direct measurement of TNT and TNT-d_3 induction times provided a t_{ID}/t_{IH} ratio indicative of a primary isotope effect equal to 1.66 over the range 245–269 °C. This rate-determining carbon–hydrogen bond rupture in the TNT methyl group ultimately must be responsible for initiating the exothermic decomposition process.

Mixing 3.7 mol % hydroquinone with TNT resulted in a substantially accelerated thermochemical decomposition, as evidenced by the disappearance of the induction period. This behavior is best explained by hydroquinone donating its more labile hydrogen atom to a TNT molecule. This strongly suggests that the rate-determining carbon–hydrogen rupture in pure TNT proceeds homolytically with transfer of a benzylic hydrogen probably to an oxygen in a nitro group. The reaction between hydroquinone would be expected to be an oxidation–reduction which is also characteristic of pure TNT thermochemical decomposition reactions. Mixing 3.7 mol % benzoic acid, a proton donor, with TNT failed to accelerate the decomposition reaction significantly. This further supports the proposed homolytic carbon–hydrogen bond rupture in the TNT methyl group.

Calculations from decay phase C data produced a large negative entropy of activation (−16.4 eu) that is consistent with the formation of a highly ordered cyclic transition species. Such a species might be generated during the degradation by a cyclic interaction between the methyl group and adjacent *o*-nitro group during either an intra- or intermolecular reaction pathway. But cyclic interactions resulting from subsequent oxidation reactions, known to proceed during this latter decay phase C, could be responsible in part or whole for the entropy of activation found.

Table IV. Hydrogen Donor Effect upon Molten TNT Decomposition (263 °C)

	TNT	3.7% BA/TNT	3.7% HQ/TNT
Induction time, s	297	272	0[a]
Time to max reaction, s	644	436	356[b]

[a] Not detectable below 120 s due to temperature equilibration time required for molten TNT. [b] This is a maximum value assuming a 120-s induction period.

This study successfully integrated the deuterium isotope effect concept with isothermal DSC analysis. It represents the first direct experimental evidence that homolytic carbon–hydrogen bond rupture in the methyl moiety constitutes the initial rate-determining step for exothermic thermochemical decomposition of liquid TNT. The mechanism of this reaction is quite complex, and additional investigation is required for a total mechanistic elucidation of neat TNT thermochemical decomposition. Studies are continuing to determine the chemical identity of the catalytic compound I and to elucidate this complex decomposition mechanism. Further investigations using isothermal DSC measured deuterium isotope effects are in progress to relate the nature of polynitro aromatic structure and bonding to a compound's stability/instability toward thermochemical decomposition processes. This successful use of deuterium isotope effects with the convenient isothermal DSC kinetic analysis technique paves the way for the direct experimental study of thermochemical mechanistic phenomena, that to date have eluded detection by other investigative techniques. Application of deuterium isotope effects to isothermal DSC analyses is limited only to the imaginative approach and insight of future investigations.

Experimental Section

General Procedures. All isothermal DSC measurements were obtained with a Perkin-Elmer Model DSC-1 instrument. The average and differential temperature settings on the DSC-1 were calibrated with a tin standard (mp 222 °C). The instrument was preheated to the desired reaction temperature for each analysis. A sealed but empty aluminum cell, Perkin-Elmer part no. 219-0062, always remained upon the reference thermal support. While the instrument thermally equilibrated, the weighed TNT samples (4.05 ± 0.05 mg) were sealed in an aluminum cell using a Perkin-Elmer sealer assembly, part no. 219-0061, that provided a cold weld of the cell lid to the pan. The loaded cell was placed upon the sample thermal support, and immediately the chart recorder scan was activated. The thermochemical decomposition reaction then proceeded to completion, and the isothermal DSC curve was evaluated for the desired data.[2-4,10] Analyses of TNT and TNT-d_3 were conducted isothermally for each compound at 245, 251, 257, 263 and 269 °C. The TNT used was synthesized by a previously developed procedure[23] and was purified by recrystallization from 95% ethanol (mp 80.0–81.2 °C). Sublimed samples afforded isothermal DSC induction times no different from the recrystallized material.

Synthesis of α,α,α-Trideuterio-2,4,6-trinitrotoluene (TNT-d_3). Into 35 mL of acetone was dissolved 5 g of TNT. Next, 10 mL of 98% D_2O was added to the solution followed by less than 1 mL of triethylamine (catalytic amount). The solution instantaneously became dark red. After stirring for 15 min at room temperature, D_2SO_4 was added dropwise until the solution was acidic (pH 3 by wide-range pH paper). The solution was extracted with $CHCl_3$ and dried over anhydrous $MgSO_4$. In vacuo solvent removal of the $CHCl_3$ afforded 4.5 g of solid product. The product was purified by sublimation to yield an off-white solid (mp 80.2–81.6 °C). Analysis by NMR indicated deuterium exchange had occurred at the methyl moiety, and mass spectrometry (M^+ 230) revealed the TNT-d_3 to be 96% isotopically pure by analysis of the *m/e* 212 and 210 fragments (base peak: TNT-d_3 212; TNT 210).

Preparation of the Mixed 3.7% Hydroquinone/2,4,6-Trinitrotoluene Sample. To ensure sample homogeneity, the 3.7 mol % HQ/TNT sample was prepared as follows. Into a 4 dr. glass vial was weighed 1.80 mg of Mallinckrodt "photo purified" hydroquinone and 100.00 mg of TNT. The mixture was dissolved in about 2 mL of Burdick–Jackson "Distilled-in-Glass" acetone, and the acetone was air evaporated. The remaining solid was thoroughly dried in a vacuum oven before being triturated into a fine powder. A pure TNT sample was also dissolved in acetone, dried, and triturated into a fine powder. Isothermal DSC analysis of this "blank" TNT sample revealed no significant difference in its thermochemical decomposition behavior compared to the untreated TNT.

Preparation of the Mixed 3.7% Benzoic Acid/2,4,6-Trinitrotoluene Sample. Preparation of the 3.7 mol % BA/TNT sample was accomplished as described for the 3.7 mol % HQ/TNT sample using 2.00 mg of benzoic acid (Eastman Organic Chemicals) and 100.14 mg of TNT.

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Registry No.—TNT, 118-96-7; TNT-d_3, 52886-05-2.

Supplementary Material Available. Figures 6–9 which are the hydrogen-substituted TNT kinetic plots analogous to Figures 2–5, respectively (4 pages). Ordering information is given on any current masthead page.

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