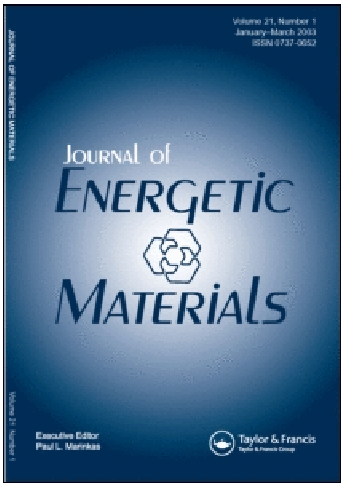

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DEUTERIUM ISOTOPE EFFECTS DURING THE THERMAL DECOMPOSITION OF 1,4-BUTANEDIAMMONIUM DINITRATE AND SELECTED COMPOSITES WITH AMMONIUM AND POTASSIUM NITRATES

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ABSTRACT

The thermal decomposition of 1,4-butanediammonium dinitrate (BDD), selected BDD-based composites with ammonium/potassium nitrates (BAK), and specifically deuterated analogs, was investigated. A previous study showed that molten BDD decomposes thermally via a multi-step process that produces a variety of condensed phase and gaseous products. The nature of the products suggested that proton transfer from cation to anion followed by C-N bond rupture occurred early in the decomposition process. During the present investigation condensed phase DSC induction period studies performed using specifically deuterated BDD analogs generally displayed inverse deuterium isotope effects. Impact

sensitivities, times to explosion and critical temperatures were also determined for BDD, the BAK composites, and many of their N-deuterated analogs. While these studies did not unequivocally reveal the specific covalent bond rupture responsible for generating the conditions favorable for exothermic decomposition, they did provide a direct relationship between induction period chemistry and macroscopic thermal sensitivity properties.

INTRODUCTION

Condensed phase kinetic deuterium isotope effect (KDIE) studies have been used successfully to elucidate the reaction mechanisms associated with the thermal decomposition of selected energetic materials. Some of the materials studied previously include 2,4,6-trinitrotoluene (TNT)[1], 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)[2], octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)[3] and hexahydro-1,3,5-trinitro-s-triazine (RDX).[4] These studies were carried out with the materials in the solid (HMX, RDX, TATB), liquid (TNT, HMX) and mixed-melt (HMX) states, using isothermal differential scanning calorimetry (DSC) and thermogravimetry (TGA) as the primary analytical techniques. Application of KDIE to relate key mechanistic features derived from quantitative laboratory experiments to the highly exothermic decomposition reactions exhibited by energetic materials appears to have been successfully accomplished.[2,5,6]

This paper describes (i) the use of KDIE to mechanistically characterize the induction period of the isothermal DSC decomposition curve for the molten energetic salt, 1,4-butanediammonium dinitrate (BDD) and (ii) the relationship of these initial mechanistic findings to the more qualitative thermal and impact sensitivity characteristics of BDD and its composites (BAK) with ammonium (AN) and potassium (KN) nitrates. These latter characteristics were derived from time to explosion and impact experiments.

EXPERIMENTAL

Isothermal DSC analyses were performed with a Perkin-Elmer DSC-4/Thermal Analysis Data Station System. Dried samples (1.55 ± 0.05 mg) were weighed into standard aluminum pans (Perkin-Elmer part number 219-0062) and sealed hermetically under an air atmosphere. The sealed sample pans were weighed before and after each experiment to insure that loss of volatiles did not occur. The induction period at each temperature is the result of a minimum of five successful experiments and is defined as the time elapsed from t=0 at isothermal temperature until the initial deflection of the exothermic acceleratory phase from the horizontal baseline.

Impact data were obtained with a Bureau of Mines Model No. 2 Impact Device. Time to explosion test apparatus and procedure have been described elsewhere.[7]

BDD-1,1,4,4-d_4 and BDD-2,2,3,3-d_4 were prepared according to the procedures described by Marchand, et al.[8] N-deuterated BDD and BAK composites were prepared by dissolving approximately 1 g of the original salt/ mixture in 5 ml of D_2O. The resulting solution was stirred for 30 min. and then evaporated to dryness. The procedure was repeated, and the resulting product was then dried to constant weight in vacuum at 50°C and stored in an inert atmosphere box. Deuterated and non-deuterated composites are designated BAK-d_x and BAK, respectively.

RESULTS

DSC Deuterium Isotope Effect (DIE) Studies

Thermolysis experiments were carried out with molten samples and are characterized by an induction period that precedes the acceleratory (exothermic) decomposition phase. During the course of this study, it was found that the occasional release of corrosive decomposition gases into the DSC cell ultimately reduced the precision of the data and shortened the cell life. In some cases a DSC cell was used for as few as two hundred experiments. This problem precluded our acquiring absolute induction times for all compounds included in this study from a single DSC cell. While absolute induction times were unique to a given DSC cell, DIE values and apparent activation energies were not cell dependent. As a result of this cell life problem, the log induction times versus reciprocal temperature data presented graphically in Figure 1 are as measured for BDD and BDD-N,N,N,N',N',N'-d_6 and normalized for BDD-1,1,4,4-d_4 and BDD-2,2,3,3-d_4. Averaged raw induction period data are presented for BAK (11 mole percent AN) and BAK-d_x (11 mole percent AN-d_4) in Figure 2. DIE values and apparent activation energies are shown in Tables 1 and 2, respectively.

Time To Explosion Experiments

Time to explosion tests were carried out on 40 mg samples of BDD, its N-deuterated analog, four BAK composites and their N-deuterated analogs. The C-deuterated analogs of BDD were not available in sufficient quantities to support time to explosion experiments. Times to explosion versus temperature curves are shown for selected materials in Figure 3 and critical temperatures are shown in Table 3. Presentation of the time to explosion data for the other BAK composites would serve only to clutter the figure. The critical temperature is defined as the lowest constant surface temperature at which a material of a specific size, shape, and composition can self-heat catastrophically.[2] Log times to explosion versus reciprocal temperature curves for BDD and its N-deuterated analog are shown in Figure 4.

Impact Experiments

Impact sensitivity experiments were carried out with four BAK and one BAK-d_x (11 mole percent AN-d_4) composites using a 2.5 kg weight. Impact sensitivity data for BDD and its N-deuterated analog were obtained using a 5 Kg weight. The materials were ground, but not sieved, prior to testing. Each powdered sample was impacted on Norton coated abrasive paper of 180 grit (FSN 5350-271-7930). Twenty-five to thirty samples were used for each complete test. BDD-1,1,4,4-d_4 and BDD-2,2,3,3,-d_4 were not available in sufficient quantities to support impact experiments. The results are presented in Table 4.

DISCUSSION

The present study has sought to use the KDIE to elucidate the chemical reaction mechanisms associated with the induction period of the isothermal decomposition curve for molten BDD. A second objective was to demonstrate the relationship of these findings to BDD's thermal and impact sensitivity characteristics and those of selected BAK composites. It has been shown that many competitive reactions take place during the induction period[9] of the BDD thermal decomposition process and it is believed that these reactions result in the accumulation of a threshold concentration of materials which catalytically initiate exothermic decomposition. This hypothesis is supported by the results of a cumulative induction period study where it was demonstrated that the induction period is afforded a "memory".[9]

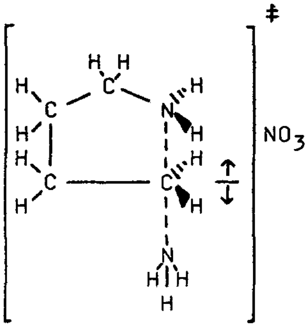
While a rate constant, $\underline{k}$, cannot be determined for the induction period, direct measurement of induction times, t, can be obtained from isothermal DSC experiments. It has been suggested[1] that the induction time is inversely proportional to the rate constant

$$\frac{k_h}{k_d} = \frac{t_d}{t_h}$$

where t_d is the induction time for a specifically deuterated material and t_h is the induction time for a non-deuterated material.

The deuterium atoms of the labeled BDD analogs used in this investigation were selectively placed around the C-N bonds, since calculational data suggest that this bond is the most likely to rupture. Politzer[10] showed by computational analysis that a

$C\text{-}NH_3^+$ bond is weaker than a $C\text{-}NH_2$ bond and, hence, is favored for C-N bond fission. Assuming that C-N bond rupture is involved in the transition state and taking into consideration the selective placement of deuterium atoms in the substrate, the observed inverse DIE values for the N- and C-deuterated analogs of BDD were unexpected. The results from a previous study,[9] suggest that a cycloelimination reaction is rate determining with respect to the induction period and leads to conditions favorable for initiation of the acceleratory phase of the decomposition process. The following structure is thought to be representative of the probable transition state associated with this reaction:



Inhibition of the C-H out-of-plane bending motion of the central carbon atom may then account for the results from BDD-1,1,4,4-d_4 and BDD-N,N,N,N',N',N'-d_6.[11,12]

Isothermal DSC experiments are carried out under carefully controlled conditions allowing the researcher to make quantitative measurements and gather data suitable for kinetics and mechanistic related determinations. Time to explosion experiments, on the other hand, are more qualitative and are designed primarily to provide the researcher with safety-related data. Safety data are required during the development of new energetic materials/formulations. These experiments typify an experimental condition considered more severe; i.e., higher temperatures, larger mass, reduced or no free volume, and more confinement, than that encountered during an isothermal DSC experiment.

The results from other studies[2] revealed an apparent correlation between the kinetic chemical reaction mechanisms gleaned from DSC experiments and observed energetic material sensitivities measured by these more qualitative macroscopic experiments. This correlation is reflected in critical temperature (T_c) differences between energetic materials and their deuterium labeled analogs. Materials whose deuterated analogs possess a higher critical temperature than the unlabeled materials also provide a normal DIE as determined by isothermal DSC analysis. These deuterated materials tend to be more thermally stable. Deuterated materials whose critical temperatures are equal to or less than those of their unlabeled analogs generally correlate with either no DIE or an inverse DIE.

The time to explosion curves for BDD and its N-deuterated analog, when plotted as log induction time versus reciprocal temperature (1/T), have greater slopes at lower temperatures (approximately 222 to 245°C) than at higher temperatures (approximately 270 to 315°C). See Figure 4. These slope changes may result from a mechanism change or may reflect a change from a heat transfer dominated process at high temperature to a chemistry dominated process at lower temperature.[13] While there are differences observed between the times to explosion of these two compounds, neither of them exhibits a measureable critical temperature. This is due to random pressure rupture of the sealed sample tubes. Even though time to explosion measurements are not as precise as critical temperature measurements, time comparisons along the entire lengths of these curves clearly show that the N-deuterated analog exhibits an inverse isotope effect except in the transition area between the two curves of differing slope where no DIE is apparent. DIE values vary between 0.7 and 1.0 from the highest temperature to the transition area, whereas the values remain almost constant (average 0.73) for the low temperature (220- 230°C) section of the curves. This average DIE value corresponds well with the 0.80 average value obtained by extrapolating the isothermal DSC induction period data shown in Figure 1 to this temperature range. These findings suggest that the same effect that controls the relatively low pressure BDD DSC induction period decomposition process in air also controls the more violent time to explosion process.

In order to determine the influence of N-deuteration on the thermal explosion characteristics of a potential composite explosive, BDD was mixed with varying amounts of an AN/KN mixture. The resulting BAK composites were deuterated specifically at all ammonium sites, and then subjected to time to explosion tests. The critical temperatures exhibited by the deuterated composites were less than those exhibited by the non-deuterated composites, and the ΔTc values ($T_{c(h)}$-$T_{c(d)}$) were essentially constant (average 11.5°C). These results are consistent with an inverse deuterium isotope effect and suggest that the decomposition mechanism is similar for all the composites considered during this investigation. An inverse DIE is also exhibited by BAK and BAK-d_x (11 mole percent AN-d_4) composites when subjected to DSC induction period experiments. The average DIE obtained from samples heated over the temperature range 195-200°C was 0.48 (see Table 1). Since the results from time to explosion tests with AN and AN-d_4 suggest the operation of a normal DIE, it is believed the overall data from these composite tests are consistent with the postulates that (i) the BDD component decomposes independently of AN, (ii) the BDD thermal degradation mechanism significantly influences times to explosion and critical temperatures of the composites, and (iii) the thermal degradation mechanism is similar for all the composites. The critical temperature data also show that the global thermal stability of the BAK composites increases markedly with increasing AN concentration. This is consistent with the above postulates in that it is reflective of the high thermal stability of AN and its participation in the overall degradation process. AN may act as an acidic diluent that inhibits the following dissociation reaction,

$$\mathrm{BDD} \rightleftharpoons \underset{\mathrm{BDM}}{[H_2N(CH_2)_4NH_3]NO_3} + HNO_3$$

and in so doing, effectively stabilizes the mixture. It has been suggested that BDM is involved in a cycloelimination reaction that leads to the formation of transient pyrrolidinium nitrate (PN) during the induction period.[9] It was demonstrated experimentally[14] that the addition of trace amounts of PN to molten BDD significantly shortens the induction period, thereby thermally destabilizing the salt. The increased thermal stability associated with the BAK composites may also be reflected in the apparent E_a values shown in Table 2, where the apparent E_a for BAK (11 mole percent AN) is somewhat greater than that for BDD. DSC induction times for BAK composites with concentrations of AN greater than 11 mole percent could not be measured due to pressure rupture of the sealed sample pans.

Impact sensitivities of the four BAK composites were shown to increase with increasing AN concentration. This trend is consistent with the findings of Kamlet[15], where an empirical relationship was shown to exist between impact sensitivity and oxygen balance for compounds with similar trigger linkages. Trigger linkage is defined as the weakest atom-to-atom bond. Kamlet[15] suggested that impact sensitivities of explosives depend on the rates of the thermal decomposition reactions which occur at the temperatures generated under the impact hammer. He concluded that the rate determining step was usually homolytic cleavage of the trigger linkage. The DIE results from experiments discussed earlier suggest the trigger linkage may reside with the BDD component, probably the $C-NH_3^+$ bond. While an inverse DIE was reflected in the impact data from the BAK and BAK-d_x composites (11 mole percent AN), there was not a sufficient difference in the H_{50} values from BDD and BBD-N,N,N,N',N',N'-d_6 to make the same inference.

Additional impact studies with a complete compliment of BDD and BAK composites and selected N- and C-deuterated analogs, carried out under carefully controlled conditions, are required before any conclusions can be drawn regarding the identification of the impact sensitive trigger linkage.

CONCLUSIONS

It has been shown from a previous study[9] that BDD decomposes thermally from the molten state via a multi-step process that produces a variety of condensed phase and gaseous products. The present study concentrated on the condensed phase DSC induction period and was carried out by using specifically deuterated BDD analogs. Inverse deuterium isotope effects were generally displayed. While this study did not unequivocally reveal the specific covalent bond rupture responsible for generating the conditions favorable for exothermic decomposition, it did provide what appears to be a direct relationship between DSC induction period chemistry and macroscopic thermal sensitivity properties. The DIE results suggest that:

a. The same effect that plays a significant role in controlling the relatively low pressure DSC induction period of the BDD thermal degradation process in air, also plays a similar role in the more violent time to explosion process.

b. BDD, when formulated into BAK composites of varying BDD concentration, appears to decompose independently of the AN/KN components by a process similar to that of pure BDD.

c. Reactions controlling the DSC induction period of the BDD thermal degradation process also appear to play a role in controlling the DSC induction periods, times to explosion, and critical temperatures of BAK composites.

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TABLE 1. DSC Induction Period Deuterium Isotope Effects For BDD and BAK(11 mole % AN) and Their Deuterated Analogs In an Air Atmosphere

	t_d/t_h			
Temp (oC)	BDD- N,N,N,N',N',N'-d_6	BDD- 1,1,4,4-d_4	BDD- 2,2,3,3-d_4	BAK-d_x (11 mole % AN)
175	0.74±0.12	----	----	----
180	0.85±0.15	----	0.47±0.05	----
185	0.69±0.10	----	----	----
190	0.84±0.15	0.52±0.03	----	----
191	0.75±0.16	----	----	----
195	0.72±0.12	0.55±0.07	----	0.51±0.05
198	----	----	----	0.47±0.08
200	0.70±0.11	0.55±0.08	----	0.45±0.08

TABLE 2. Induction Period Apparent Activation Energies

	Apparent E_a(1) (Cal/Mole)	Temp Range (°C)
BDD	22400 ± 1316	200-170
BDD-N,N,N,N',N',N'-d_6	21542 ± 2035(2)	200-175
BDD-1,1,4,4-d_4	17120 ± 1680	200-190
BDD-2,2,3,3-d_4	26970 ± 1590	180-170
BAK (11 mole % AN)	24320 ± 3360	200-195
BAK-d_x (11 mole % AN-d_4)	27170 ± 2910	200-195

(1) Apparent activation energies for the DSC induction periods are derived from the slope of log time versus reciprocal temperature curves generated from raw data only.

(2) This apparent E_A value is derived from the seven data points used to calculate the DIE values in Table 1. Removal of the induction time for 180°C, which appears to be a high time value, changes the apparent E_A to 19476 ± 976 Cal/Mole.

TABLE 3. Critical Temperature Data For BAK/BAK-d_x Composites

Composite/Compound	Critical Temperature (^oC)
BDD	$<222^{(1)}$
BDD (N-deuterated)	$<222^{(1)}$
BAK (11.0 mole % AN)$^{(2)}$	239
BAK-d_x (11.0 mole % AN-d_4)	230
BAK (35.8 mole % AN)	244
BAK-d_x (35.8 mole % AN-d_4)	230
BAK (55.2 mole % AN)	264
BAK-d_x (55.2 mole % AN-d_4)	253
BAK (77.1 mole % AN)	279
BAK-d_x (77.1 mole % AN-d_4)	267

(1) Critical temperature could not be determined.

(2) Mole percent KN in the above BAK composites is 2.6, 6.3, 7.8 and 10.8, respectively.

TABLE 4. Impact Sensitivity Data For BDD-Based Composites

Composite/Compound	OB_{100}	H_{50}(cm)(1)
BAK (11.0 mole % AN)	-4.21	124
BAK (35.8 mole % AN)	-2.96	82
BAK (55.2 mole % AN)	-1.62	100
BAK (77.1 mole % AN)	+0.99	49
BDD	-4.67	95(2)
BDD-*N*,*N*,*N*,*N'*,*N'*,*N'*-d_6	-4.67	88(2)
BAK-d_x (11.0 mole % AN-d_4)	-4.21	75

(1) Reference 15

(2) 5 Kg hammer

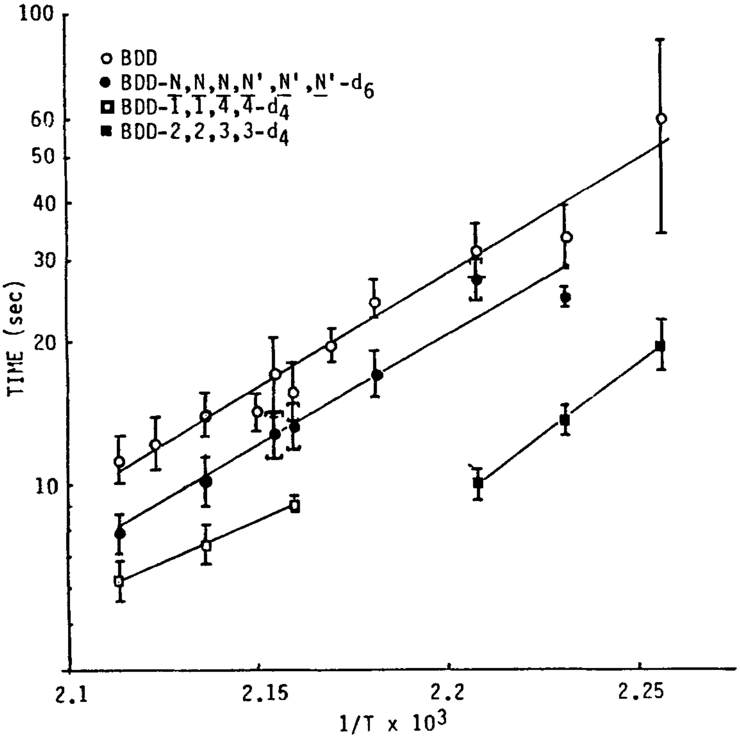

FIGURE 1. Induction Times for Air Versus Inverse Temperature ($^{o}K^{-1}$) for BDD and its C- and N-deuterated Analogs.

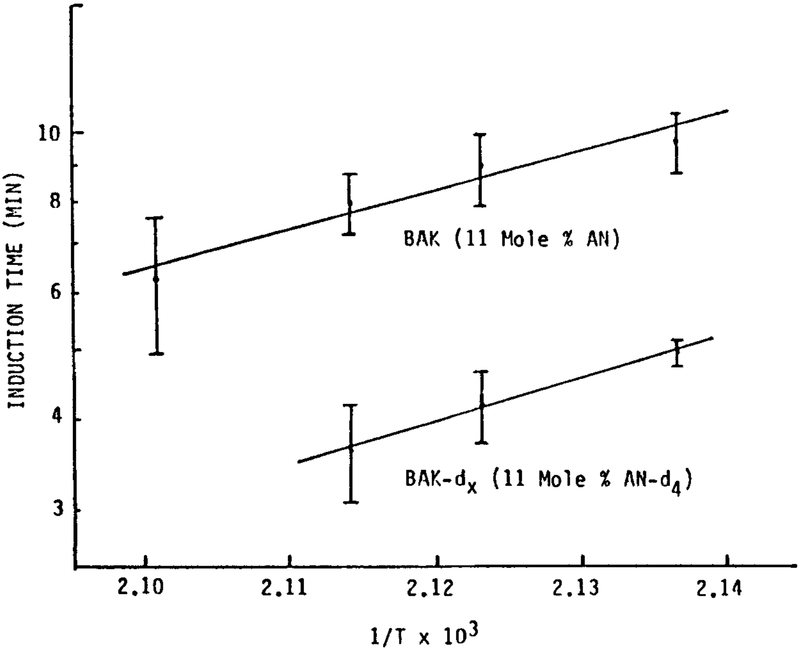

FIGURE 2. Induction Times for Air Versus Inverse Temperature ($^oK^{-1}$) for BAK (11 Mole Percent AN) and BAK-d_x (11 Mole Percent AN-d_4)

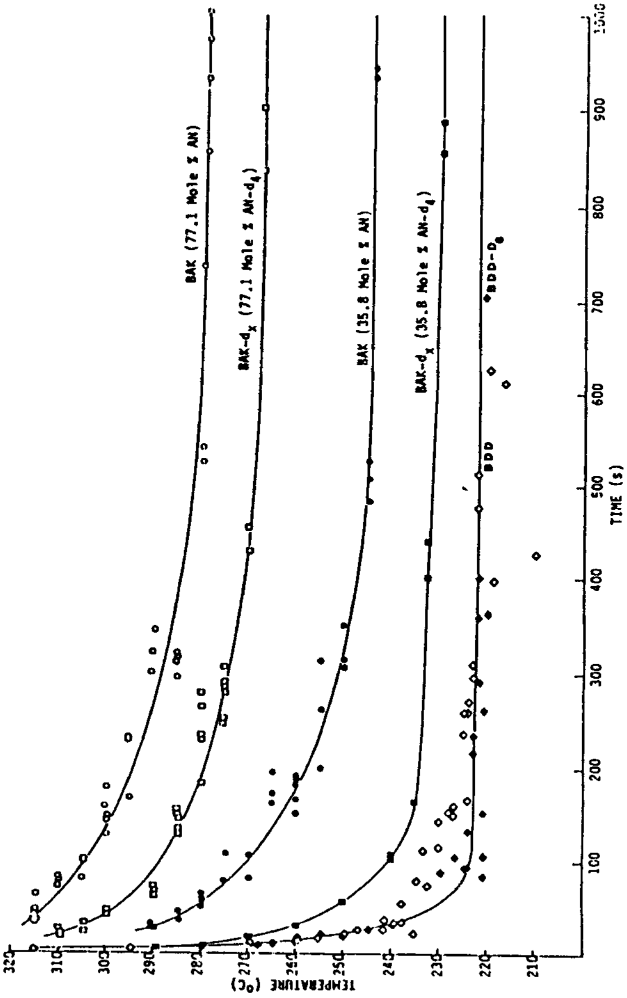

FIGURE 3. Experimental Time to Explosion Curves for BDD, BAK (35.8 Mole Percent AN), BAK (77.1 Mole Percent AN) and Their N-Deuterated Analogs.

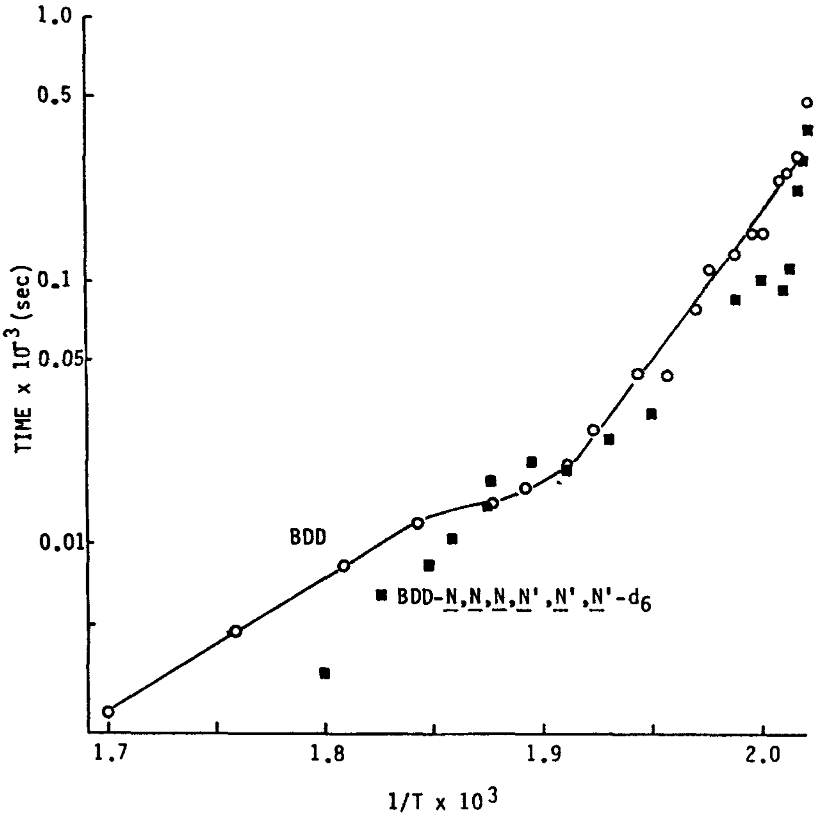

FIGURE 4. Experimental Time to Explosion Curves for BDD and its N-deuterated Analog Plotted as Log Time vs. Reciprocal Temperature.

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