KINETIC-ISOTOPE EFFECTS IN THERMAL EXPLOSIONS

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ABSTRACT

Kinetic-isotope effects can be used to detect the specific functional groups involved in the elementary reactions of complex explosives decomposition processes. Isothermal kinetics methods must be used to correlate component reactions with specific reaction regimes. When component reactions can be identified at different temperatures, kinetics constants can be determined. Conditions for self heating to explosion can be calculated from the kinetics constants, and predictions can be tested against independent time-to-explosion measurements.

The sign of the volume of activation can be predicted from the magnitude of the kinetic-isotope effect. When the sign of the volume of activation is known, it is possible qualitatively to predict pressure effects on chemical reaction rates. An ability to predict pressure effects on rates is important in predicting the relative sensitivities of different explosives.

Kinetic-isotope effects can be observed with time-to-explosion experiments, and the specific component reaction responsible for thermal explosion can be identified.

INTRODUCTION

We have made kinetics measurements on a large number of high-energy materials and mixtures, and we have yet to observe a simple decomposition. Very few reactions involve only a single step, and changes in mechanism are common. In order to develop predictive models for the thermal hazards of high-energy materials, it is necessary to identify the component reactions of complex decomposition processes that are responsible for self heating to explosion, and kinetics constants must be measured for those specific component reactions. It is erroneous and dangerous to base hazards predictions on a single set of kinetics constants that is supposed to describe a complete decomposition process when mechanisms change during the course of the decomposition.

When the kinetics of complex reactions must be measured, it is helpful to eliminate as many variables from the process as possible. Kinetics measurements can be interpreted with greatest confidence when rate observations are made at constant temperature and pressure. Unfortunately, system-depen-

dent predictive models may be produced by using kinetics constants obtained at a constant low pressure. Ordnance systems that are heavily confined and/or pressurized may be more hazardous than such models would predict.

Kinetic-isotope-effect (KIE) measurements can profitably be applied to studies of high-energy-materials hazards in two ways: they can be used to correlate specific component reactions with specific reaction regimes as observed by rate measurements, and they can be used to prove that specific reactions are important in thermal explosion. Our method for hazards evaluations on complex systems involves both rate measurements and independent time-to-explosion measurements with normal and isotope-labeled materials. Erroneous predictive models for thermal hazards can be identified with some confidence.

KINETICS CONSIDERATIONS

Reaction rate and amount of reactant(s) are the fundamental data required for a kinetics study. All chemical reactions involve energy; therefore, energy evolution or absorption can provide the basis for kinetics measurements. The rate of heat evolution will be exactly proportional to the rate of the (global) chemical reaction(s) at any instant as follows

$$dq/dt = Q\, d\alpha/dt = kQf(\alpha) \tag{1}$$

where dq/dt is the rate of heat evolution, Q is the heat of reaction, α is the fraction decomposed, $f(\alpha)$ is some depletion function that results from the mechanism(s) of the process, and k is the chemical rate constant.

Although heat evolution and rate are proportional, changes in mechanism associated with complex reactions can cause changes in heat of reaction (Q) and the depletion function [$f(\alpha)$] as the reaction proceeds. This means that there may not be agreement between the total amount of heat evolved at any time and the amount of reactant consumed (α). When mechanisms change during the course of a reaction, it is not valid to "linearize" the rate data to obtain a single rate constant for the entire process. A single function that will model a reaction or a specific part of a reaction is a necessary but not sufficient proof of a consistent mechanism. If the same function can be used to model the same part of a reaction over a wide range of temperatures, it is much more likely that the function is modeling a consistent mechanism. However, specific isotope labeling can often be used to identify consistent component reactions in a complex process and give indications of mechanisms.

Shackelford et al. [1] used kinetic-isotope effect to identify the position and type of attack involved in the elementary reaction in the complex decomposition of TNT (2,4,6-trinotrotoluene). They provided the first direct

experimental evidence that "homolytic carbon–hydrogen bond rupture in the methyl moiety constitutes the initial rate-determining step for the exothermic thermochemical decomposition of liquid TNT".

Experimental, data-acquisition, and data-evaluation improvements in isothermal DSC kinetics methods and thermal-explosion testing now enable quantitative applications of KIE methods to thermal-safety problems.

Predictive models for rate as a function of temperature can be made with confidence only for consistent reactions. Even when extremely complex systems are encountered, consistent regimes of reaction can often be identified at very early times (before significant depletion has occurred) and at late times when steady state has been achieved. Kinetics constants for initial reactions may have some chemical significance, providing measurements of the energetics of simple processes, but kinetics constants for complex reactions are nothing more than temperature coefficients of the rate.

When a specific functional group in a system under study is modified by isotope substitution, it is often possible to identify a consistent reaction regime from the magnitude and duration of the KIE in rate measurements. The type of KIE and the knowledge that a specific functional group was isotope labeled give information on the mechanism [2].

The assumption is often made that a specific process will obey a rate law of the form

$$d\alpha/dt = k(1 - \alpha)^n \tag{2}$$

where n is the reaction order. When working with condensed-phase, exothermic processes, the assumption is not often true. A law of this type requires that the maximum rate be achieved at the instant the process starts (at $t = 0$).

Autocatalytic-type behavior, typified by reaction regimes that show increasing rates with reactant depletion, is observed in most exothermic, condensed-phase reactions. Figure 1 shows rate curves typical of energetic materials. Isothermal rate curves like these can be results of chemical autocatalysis, depletion of a stabilizer, melting with decomposition, or solid-state reactions. All degradation processes involving organic explosives and propellants that we have observed have involved autocatalytic-type processes, and none of them has shown a single, consistent mechanism throughout. Melting, polymorphic transitions, and/or changes in composition are usually responsible for observed changes in mechanism. Figure 1 shows that the earlier rate processes in the TATB (1,3,5-triamino-2,4,6-trinitrobenzene) decomposition are changed significantly by substitution of deuterium for hydrogen in all of the amino groups. The rate change makes it possible to identify the early reaction regime that has a consistent mechanism. It can be seen that the final decomposition process is not affected by deuterium substitution.

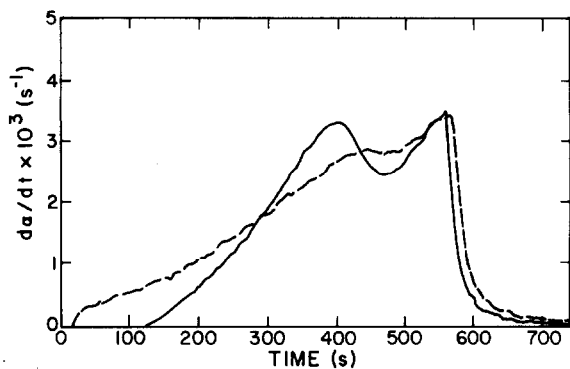All autocatalytic-type reactions will show order plots [3] with early reac-

Fig. 1. Isothermal DSC rate curves from TATB-H$_6$ (———) and TATB-D$_6$ (— — —) at 630 K. The curves have been normalized to the equivalent of a 1-mg sample with a DSC range of 1 mcal s^{-1} full scale.

tion regimes having negative slopes (negative apparent reaction orders). Abrupt changes in slope prove changes in mechanism, and stoichiometric information can often be obtained from the position of a discontinuity [4]. Autocatalytic-type depletion functions can often be found that will accurately model rate data from reaction regimes showing curved, negative-slope order plots [5].
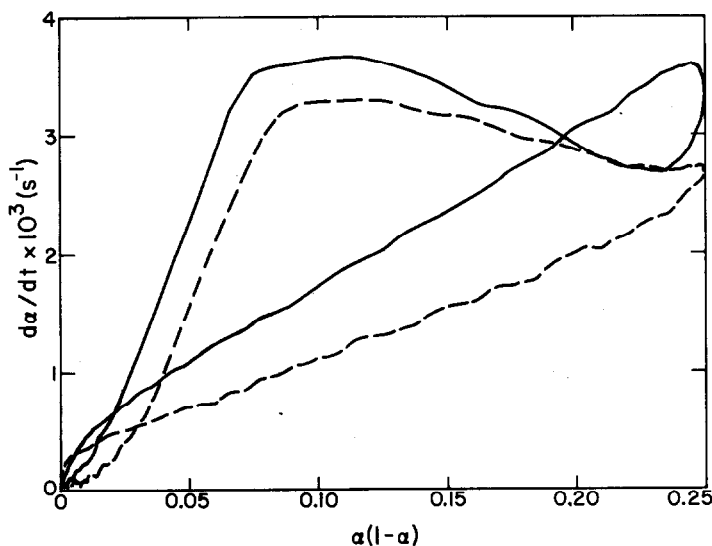

Fig. 2. Autocatalytic-rate-law plots of the rate data from Fig. 1. The rate law used is $d\alpha/dt = k\alpha(1-\alpha)$. Slopes of straight-line portions are rate constants for those reaction regimes. The earlier part of the process corresponds to the long, positive-slope, straight-line portion. The plot reflects back on itself at $\alpha = 0.5$ where $\alpha(1-\alpha) = 0.25$. The difference in slope provides the value of the kinetic-isotope effect for the specific consistent component reaction (k_H/k_D). ———, TATB-H$_6$; — — —, TATB-D$_6$.

Figure 2 shows that the first 50% of the global TATB decomposition can be modeled accurately with a simple $d\alpha/dt = k\alpha(1 - \alpha)$ rate law. It can also be seen that the last $5 - 15\%$ of the decomposition shows a different linear slope (has a different rate constant, k). The linear nature of the early and late segments indicates consistent reactions; however, the fact that the entire first 50% of the process shows a different linear slope with deuterated TATB proves a consistent mechanism involving amino groups. Rate constants obtained from the consistent mechanisms at different temperatures can be used with some confidence for the calculation of kinetics constants.

THERMAL INITIATION

When accurate kinetics constants can be measured for the consistent component reactions of a complex process, thermal-hazards predictions can be made. However, it is extremely important to recognize the fact that the kinetics constants used must actually correspond to the component reaction involved in the phenomenon to be predicted. For example, if a slow induction process is involved in the decomposition of an explosive, the time required for self heating to explosion will largely be determined by the kinetics of the induction process. Kinetics constants measured for a maximum-rate process will not often provide an accurate prediction of time to explosion. The effects of specific component reactions on the thermal-explosion properties of an explosive can be observed by using isotope-labeled samples in time-to-explosion tests.

One value must be predicted to enable safe practical applications of explosives and other high-energy materials: it is the critical temperature for any specific size and shape (T_c). 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. The critical temperature is determined by the balance between rates of heat generation from chemical reactions and rates of heat dissipation by physical processes. It can usually be predicted according to the Frank-Kamenetskii equation [6]

$$\frac{E}{T_c} = R \ln\left[\frac{a^2 \rho Q Z E}{T_c^2 \delta \lambda R}\right] \tag{3}$$

where E and Z are the Arrhenius activation energy and pre-exponential, R is the gas constant, T_c is the critical temperature, a is a dimension (radius of a sphere or infinite cylinder or half thickness of an infinite slab), ρ is the density, Q is the heat of reaction, λ is the thermal conductivity, and δ is a shape factor (0.88 for infinite slabs, 2.0 for infinite cylinders, and 3.32 for spheres). If the kinetics constants determined for a specific consistent reaction involved in an explosive's thermal decomposition enable accurate

prediction of the critical temperature for a known size and shape of the material, the kinetics constants must describe the process responsible for catastrophic self heating.We use a simple, laboratory-scale time-to-explosion test for independent confirmation of kinetics-based thermal-hazards predictive models [7]. Isotope labeling enables correlation of measured reactions with specific thermal-explosion phases.

EXPERIMENTAL

Procedures

Isothermal DSC kinetics curves were produced and evaluated by methods similar to those described in ref. 3. Time-to-explosion test apparatus and procedures were described in ref. 7.

Samples

The TATB-H_6 and TATB-D_6 samples were made by D.G. Ott of this laboratory by amination of dichlorotrinitroanisole with either NH_3 or ND_3. Both samples were carefully recrystallized from diphenyl ether.

The DINGU (dinitroglycoluril) samples were prepared by D.G. Ott and M.M. Stinecipher of this laboratory. The DINGU-D_2 was prepared by isotope exchange from a $D_2O/DMSO/D_2SO_4$ solution by precipitation with D_2O. The DINGU-D_2 sample was recrystallized from DNO_3. The DINGU-H_2 sample was recrystallized from HNO_3.

The PETN (pentaerythritol tetranitrate) samples were prepared by M. Schwartz, M.D. Coburn, D.G. Ott, and B.W. Harris of this laboratory. The PETN-H_8 was prepared via the dibenzal derivative of pentaerythritol to eliminate higher ethers. The PETN-D_8 was prepared from deuteroformaldehyde (D_2CO) and deuteroacetaldehyde (D_4C_2O). The perdeutero-pentaerythritol was nitrated with HNO_3 without isotope exchange. Both samples were reprecipitated from acetone–water.

Small amounts of impurities, differences in crystal habit, differences in crystal perfection, and particle-size differences may cause significant differences in the sensitivity and thermal-explosion properties of explosives. In order to make isotope effect measurements as accurately as possible, we have attempted to produce the final samples in as nearly as possible identical states of perfection and purity.

RESULTS AND DISCUSSION

Observations of decomposition residues quenched at different stages of reaction prove that the entire TATB decomposition proceeds in the solid

state within the temperature range used for our kinetics measurements (570–655 K). The autocatalytic-rate-constant plots of Fig. 2 show that the earliest solid-state reaction is consistent for approximately 50% of the energy evolution, and the KIE shows that it involves the amino functional groups. Rate-constant determinations through the entire temperature range showed the same consistent reactions through the same extent of reaction.

Extensive measurements gave the following kinetics constants for the first consistent, solid-state decomposition reaction of TATB-H_6: $E = 59.1$ kcal mole^{-1} and $Z = 3.75 \times 10^{18}$ s^{-1}. The k_H/k_D ratio was found to be about 1.5.

The fact that $k_H > k_D$ proves that the KIE is a "normal" isotope effect, and the size indicates that it is a "primary" effect [1,2]. The most likely interpretation of the results is that the elementary reaction involves motion of the hydrogens.

Figure 2 shows that the final reactions of TATB-H_6 and TATB-D_6 are identical. This is to be expected from elemental analysis results, because the sample is nearly devoid of hydrogen during the final reaction phase.

Figure 1 shows that the TATB rate curves contain two maxima. The overall (global) process appears to involve two consecutive, autocatalytic-type, solid-state reactions that do not attain steady state. At higher temperatures the first maximum is higher than the second. Since the first maximum is reached by a single, solid-state, consistent reaction, the same kinetics constants should describe both the critical temperature and time to explosion. This should be true only for pure TATB, because impure TATB shows initial-rate processes that can be correlated with impurity levels. It cannot be assumed that the same mechanism will control both the critical temperature and time to explosion for all explosives and propellants.

Figure 3 shows the experimental time-to-explosion curves obtained from the recrystallized TATB-H_6 and TATB-D_6. The measured critical temperature for TATB-H_6 is 354°C; that for TATB-D_6 is 366°C. The significant reduction in rate that results from deuteration of the amino groups of TATB (observed by the kinetics measurements) is reflected in the higher critical temperature of TATB-D_6. This fact proves that there is a large contribution made to the processes involved in self heating to explosion by the consistent, solid-state reaction that we observed and measured. The extent of the contribution can best be determined by comparing calculated and experimental critical temperatures. Time-to-explosion measurements are not so precise as critical-temperature measurements.

All of the values except heat of reaction (Q) that are necessary for the calculation of T_c with eqn. (3) can be measured directly. The sample thickness in the time-to-explosion test averaged 0.065 cm for TATB-H_6; therefore, $a = 0.033$ cm. The density (ρ) was calculated from sample dimensions to be 1.81 g cm^{-3}. The thermal conductivity of TATB has been measured as 1×10^{-3} cal cm^{-1} s^{-1} K^{-1}, and the test geometry can be modeled as a slab ($\delta = 0.88$).
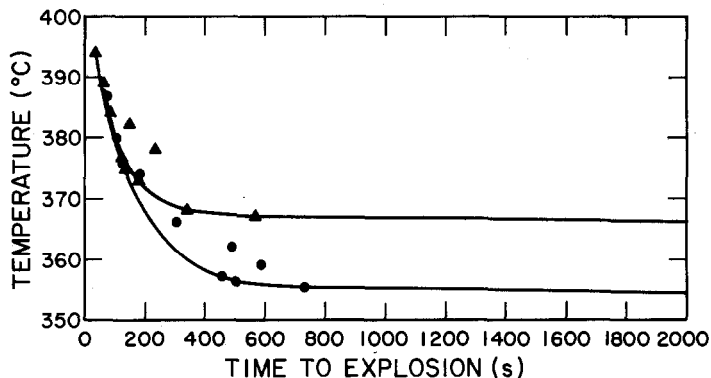
Fig. 3. Experimental time-to-explosion curves for TATB-H$_6$ (●) and TATB-D$_6$ (▲). No-go points are not shown. No explosions were obtained with TATB-H$_6$ below 354°C, and none were obtained with TATB-D$_6$ below 366°C.

The heat of reaction (Q) used in eqn. (3) must be the effective heat release under the conditions of the self-heating experiment; therefore, it is not accessible to direct measurement. Thermal reactions do not normally proceed as far toward completion as detonation reactions, and we expect Q to be less than the heat of detonation (calculated to be 1080 cal g^{-1} for TATB to H$_2$O(g) [8]). DSC measurements have shown that changes in confinement change Q without appearing to change the kinetics of the elementary decomposition reaction. Values of Q between 260 and 850 cal g^{-1} have been measured for TATB under different conditions [9]. We have previously used a value of 600 cal g^{-1} for the Q of TATB [7], and we believe that it is a good compromise value for the degree of confinement used in our time-to-explosion test.

When the above values and the measured kinetics constants are used in eqn. (3), the calculated T_c for TATB-H$_6$ is found to be 354°C. This agreement confirms our belief that we have identified and measured the kinetics constants for the reaction that controls the critical temperature for pure TATB. Additional confirmation that the measured reaction controls thermal explosion can be obtained by showing that the predicted change in the critical temperature results from deuteration.

Isotope substitution does not change the potential-energy surface for a molecule, and it does not change the potential-energy surface for any reaction of the molecule. Changes in rate result from changes in vibrational energies between the unsubstituted and substituted molecules. If $k_H/k_D \approx$ 1.5, the zero-point level [2] of TATB-D$_6$ is about 0.5 kcal below that of TATB-H$_6$. The activation energy for TATB-D$_6$ should be about 59.6 kcal mole^{-1}. Making that change in the predictive model, we calculate a T_c of 635 K. This value is in good agreement with the experimental value of 639 K, and we believe that it confirms the relationship between the reaction

observed with the DSC and the reaction responsible for self heating to explosion.

The energy-evolution rate of the first consistent reaction of pure TATB obeys a $d\alpha/dt = k\alpha(1 - \alpha)$ rate law. Its integrated form is

$$\ln\left(\frac{\alpha}{1-\alpha}\right) + C_0 = kt \qquad (4)$$

where C_0 is the constant of integration. The maximum rate (explosion) should be attained at $\alpha = 0.5$ where $-C_0 = kt$. If C_0 is indeed a constant through the temperature range used in the time-to-explosion test, the measured kinetics must largely determine times as well as critical temperatures. Although there is considerable scatter in the data of Fig. 3, $C_0 = 7.0$ with a standard deviation of 1.1 and no significant correlation with temperature. Most of the temperature-dependent change in time-to-explosion results from the temperature-dependent change in the measured rate process.

Some types of isotope effects in thermal initiation that are different from those of TATB are shown in Figs. 4 and 5.

PETN is a sensitive explosive [8,10]. Preliminary drop-weight impact sensitivity measurements on limited amounts of material indicate that there is no significant difference in sensitivity between PETN-H_8 and PETN-D_8. Figure 4 shows that there is no significant difference between the critical temperatures of the two samples; however, there is a significant difference between times to explosion.

DINGU is a moderately insensitive explosive [11]. Figure 5 shows a comparison between the time-to-explosion curves obtained from DINGU-H_2 and DINGU-D_2. Although there is only a 6°C critical-temperature difference between the two samples, time-to-explosion differences are much greater than observed with either TATB or PETN.

We believe that isotope effects in kinetics measurements and thermal-explosion experimentation will make it possible to separate and describe the
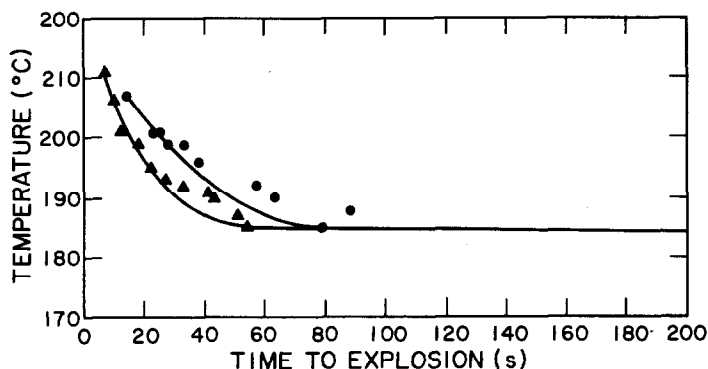

Fig. 4. Experimental time-to-explosion curves for PETN-H_8 (▲) and PETN-D_8 (●). No-go points are not shown. No explosions were obtained with either material below 183°C.
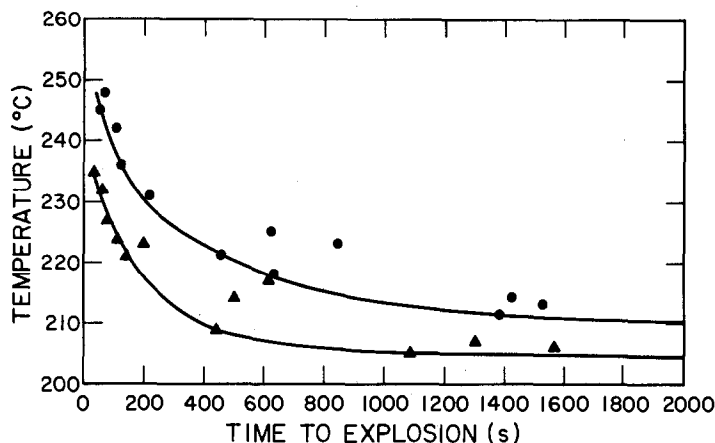
Fig. 5. Experimental time-to-explosion curves for DINGU-H_2 (▲) and DINGU-D_2 (●). No-go points are not shown. No explosions were obtained with DINGU-H_2 below 204°C, and none were obtained with DINGU-D_2 below 210°C.

components of the complex reactions responsible for the very different characteristics of different explosives and propellants.

Pressure effects

Changes in pressure can change the rates of gas-phase reactions between primary reaction products from the thermal decomposition of high-energy materials; they can also change rates of heterogeneous reactions between gas-phase products and the condensed phase. Pressure changes can also cause changes in phase-transition temperatures, and reaction rates can be greatly different in different phases. Large differences in heats of reaction are observed in most explosives as a function of confinement. Rate differences in reactions involving gas phases can be explained in terms of the Law of Mass Action. Rate differences involving different phases can be explained in terms of mechanism changes and/or differences in the internal energies of the phases [12].

Pressure effects on the elementary reaction can be explained in terms of transition-state theory [13]. It can be shown that the rate depends on pressure according to the expression

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = - \frac{\Delta V^{\ddagger}}{RT} \tag{5}$$

where $\Delta V^{\ddagger}$ is the volume of activation. The volume of activation is defined as the difference in molar volume between the reactants and the activated complex. Pressure applied to a system that has a positive volume of activation decreases the rate of the reaction; pressure applied to a system that has a negative volume of activation increases the rate.

Chaiken [14] mentioned activation volume in the context of explosives initiation, and Pastine et al. [15] have more recently reviewed the problem and discussed some theoretical aspects of pressure effects on monomolecular and bimolecular reactions. Unfortunately, unequivocal values for $\Delta V^{\ddagger}$ do not exist for explosives, and it is impossible to predict whether pressure will accelerate or decelerate initiation reactions without knowing at least the sign of the volume of activation. We believe that the sign of $\Delta V^{\ddagger}$ can often be inferred from KIE results.

"Isotope effects are essentially determined by changes in the force constants describing motions at the position of isotopic substitution for the process leading from reactant to transition state [2]." A decreased force constant can be correlated with a normal isotope effect, and an increased force constant can be correlated with an inverse effect.

If there is a decrease in the force constant, bond lengths at the positions of substitution should be greater in the transition state: $\Delta V^{\ddagger}$ should be positive. Therefore, a normal KIE ($k_H > k_D$) indicates a positive $\Delta V^{\ddagger}$ and a reaction that should be decelerated by increasing pressure. We propose that this observation will make it possible to predict which new high-energy compounds are potentially intrinsically insensitive explosives.

All other factors being equal, an explosive with a positive volume of activation will be more difficult to initiate with a shock wave than an explosive with a zero or negative volume of activation. The shock-wave pressure will reduce the rate of the elementary chemical reaction, reducing the rate at which energy is fed into the advancing wave.

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