

CALORIMETRIC STUDIES OF THE THERMAL EXPLOSION PROPERTIES
OF AROMATIC DIAZONIUM SALTS

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The critical parameters describing thermal explosion have been calculated, by means of the theory of Frank-Kamenetskii, for ten aromatic diazonium salts from enthalpic and kinetic measurements made with a differential scanning calorimeter (DSC). The work suggests that the determination of critical radii and induction times to thermal explosion could provide a convenient method of assessing the thermal behaviour of unstable compounds in practical conditions.

INTRODUCTION

Thermal explosion theory as developed initially for the ignition of certain gas mixtures (1,2), now finds applicability in the thermal explosion of the condensed phase (3). Bowes (4) has demonstrated the suitability of the Frank-Kamenetskii theory (2) in determining the critical conditions for thermal explosion of benzoyl peroxide. Merzhanov (5) has used thermal explosion and ignition theory for formal kinetic studies of exothermic reactions in the condensed phase.

In general, any exothermic reaction under the right conditions of temperature and confinement would lead to a thermal explosion. The conditions under which such explosions could occur are well documented and it is possible to calculate the critical parameters such as temperature and dimensions which determine their occurrence. There are a number of tests designed specifically to determine these parameters. Most important amongst these are the adiabatic storage test (6,7) as performed using the accelerating rate calorimeter (ARC), and the isothermal storage test (4). More recently Groothuizen et al (8) have developed a homogeneous explosion test in which the pressure effects of thermal explosion under a given amount of confinement are studied. Hutgerink (9) has developed an exothermal decomposition meter which in relation to the mass of sample used on the apparatus has a greater relative sensitivity than the differential thermal analyser (DTA) and differential scanning calorimeter (DSC), and finds applicability in determining critical parameters on a relatively large sample.

With the emergence of an ever increasing number of potentially hazardous chemicals from the point of view of storage and transportation, the desirability of having convenient and reliable forms of hazard assessment is

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important. This requirement could be partially fulfilled by a screening technique from which it would be possible to make judgements based on certain physical and chemical properties of a compound. Such assessments could form the basis for a further more detailed examination if necessary.

THEORY

This study makes use of the Frank-Kamenetskii equation which can be written in the form:

$$\delta = r^2 \rho \Delta H k_0 E \exp(-E/RT_a) / (\lambda R T_a^2) \quad (1)$$

where δ Frank-Kamenetskii dimensionless parameter, ρ the density of the sample (kg m^{-3}), ΔH the enthalpy of decomposition (J kg^{-1}), k_0 the Arrhenius frequency factor (s^{-1}), E the Arrhenius activation energy (J mol^{-1}), R the universal gas constant = $8.306 \text{ J deg}^{-1}\text{mol}^{-1}$, T the ambient temperature (K), λ the thermal conductivity of the sample ($\text{J s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$) and r the radius of a spherically or cylindrically shaped sample or the thickness of a slab shaped sample (m).

The dimensionless parameter δ arises from the stationary equation of heat conductance with continuous distributed sources of heat. The solution of this equation gives a value of δ for every steady state temperature distribution up to a maximum value δ_{max} . For values of δ in excess of δ_{max} no such solution exists and δ_{max} is identified with the critical explosion condition δ_{crit} . The values of δ_{crit} have been calculated using the numerically integrated form of eqn. 1, for an infinite slab, infinite cylinder and sphere and are 0.878, 2.000, 3.320 respectively. Values of δ for other two and three dimensional shapes have also been determined, and are given in the literature (10). (2)

It is possible to determine the dependence on the ambient temperature of the critical radius of a sample that gives a thermal explosion. There are two ways in which this can be approached. Bowes (4) used the direct approach of varying the radius of a cylindrically shaped charge and measuring the lowest ambient temperature at which thermal explosion occurred. He found that the data followed the form

$$\ln (T_a^2/r^2) = -E/RT_a + K \quad (2)$$

where K is a constant.

It was found that this equation was a re-arranged form of the Frank-Kamenetskii equation.

Another approach, which is the one used in these investigations, is to determine values for, ρ , ΔH , k_0 , E and λ . By substituting these values into equation 1 the critical ambient temperatures of thermal explosion for different shapes and sizes of samples are calculated. The DSC can be used to determine values of ΔH , k_0 and E ; depending on the complexity of the decomposition it may be necessary to operate in both the isothermal and programmed rate of temperature rise modes in order to obtain values of the required parameters. For the decomposition of substances which exhibit self

accelerating reactions, it will be necessary to carry out thermal decomposition isothermally and to fit the data to the equations that best describe such behaviour. Many organic solids decompose in a manner which can be described by an equation derived by Prout and Tompkins (11) for autocatalytic reactions; Vaughan and Phillips (12) found this to be true for the decomposition of 2-nitrobenzene 4-diazo-1-oxide. The equation takes the form:

$$\ln [x/(1-x)] = kt + c \quad (3)$$

where x = fraction decomposed.

The rate constant k , which is determined for the accelerating and decaying periods of reaction, is a function of temperature obeying the Arrhenius law and can be written as:

$$k = k_0 e^{-E/RT} \quad (4)$$

Values of k_0 and E can be determined from equation 4 from plots of $\ln k$ vs $1/T$.

For a decomposition that seemingly follows a first order path, there are convenient forms of equations for describing the data (13-15) from a temperature programmed decomposition. The one chosen for this study is that derived by the author (16) which numerically evaluates an integral form of the rate equation. The equation is of the form:

$$\ln(1-x_2) - \ln(1-x_1) = \frac{Ek_0}{RB} \int_{E/RT_2}^{E/RT_1} (e^{-u}/u^2) du \quad (5)$$

where $u = E/RT$, x_1 and x_2 are two consecutive measurements of fraction of decomposed at temperatures T_1 and T_2 respectively, and B is the programmed rate of temperature rise. Values of the Arrhenius parameters are obtained from the most linear plot of $\ln(1-x_2) - \ln(1-x_1)$ versus the numerical evaluation of the integral in eq5 in which values of E have been estimated.

EXPERIMENTAL

Work was carried out on ten solid aromatic diazonium salts all of which were of a purity which varied from 94.2 to 99.9%: these salts are listed in the first column of Table I.

Thermal conductivity measurements were made using an adaption of a Lees and Chorlton disc apparatus. Bulk density measurements were also made on the discs prepared for the Lees and Chorlton apparatus. It is assumed for the purposes of this present work that the measured values of bulk density and thermal conductivity are within 10% of those that would be encountered in large samples. A 10% difference would result in only a 5% error in the determination of the critical radii. Furthermore, an increase in the bulk density of large samples above the measurements made here would be compensated partly by an increase in thermal conductivity due to the smaller air spaces between crystals.

The enthalpy of decomposition (ΔH) and the Arrhenius parameters k_0 and E were determined from data obtained using a Perkin-Elmer DSC-2 apparatus which was operated in both isothermal and temperature programmed modes. Measurements of kinetic parameters were made on one milligramme samples encapsulated in an aluminium container of bursting pressure of 2.1×10^{-4} kg m^{-2} .

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An Indium standard was used to calibrate the DSC apparatus for the enthalpy measurements that were made on a number of weighed samples.

RESULTS

The values for thermal conductivity and density have been presented in the appendix I. There are only small variations in the values of thermal conductivity from one compound to another with an approximate mean value of $2.98 \text{ Js}^{-1} \text{ m}^{-1} \text{ K}^{-1}$. This approximate mean value is in reasonable agreement with those for organic solids of similar physical and chemical structure given in tables of physical and chemical constants.

The values of the Arrhenius parameters for six diazonium salts obtained from the programmed heating mode of the DSC, together with the enthalpy of decomposition obtained from peak measurements are shown in Table I. The linearity of kinetic data for all the decomposition are good and seem to indicate that decomposition follows a first order process. The decomposition of the four remaining compounds by the programmed heating mode did not follow first order kinetics but showed an acceleration in rate with temperature rise greater than would be expected. The Arrhenius parameters are shown in Table I and were obtained from the decomposition studies with the DSC in the isothermal mode followed by analysis of experimental data using the Prout and Tompkins equation for autocatalytic reactions; the fit of the experimental data to the theoretical curves for all the decomposition studied was good as indicated by correlation coefficients of 0.98 and better for all compounds.

The induction time to maximum rate of decomposition was measured for four of the diazonium salts with the DSC operating in the isothermal mode over a range of temperatures. It was found that there was a satisfactory proportionality between the natural logarithm of the induction time and the reciprocal of absolute temperature. This is in agreement with the equation proposed by Garner (17) for defining the induction time before thermal decomposition proceeds at an appreciable rate. The equation is as follows:

$$\log_e t(\text{induction}) = B - E/RT \quad (6)$$

where B is a constant characteristic of the compound.

Activation energies obtained from the slopes of these plots are given in Table I; in all cases there was satisfactory agreement with the values of activation energy obtained from the kinetics studies using DSC.

The calculated critical radii and extrapolated induction times for maximum rate at 293 and 328 K are given in Table II. The critical radii have been calculated on the assumption of a spherically shaped sample; the calculation of the critical radii of a cylindrically shaped sample of infinite length requires multiplication of each of the values in Table II by 0.776, which is the ratio of the square roots of the dimensionless parameters δ cylinder and δ sphere.

DISCUSSION

All the compounds studied are exothermic with heats of decomposition, on average, one sixth of the heat of decomposition of tri-nitrotoluene. With the low thermal conductivity which is characteristic of many solid organic compounds, all compounds will be expected to 'self-heat' if the sample size and shape and ambient temperature are right and if the critical conditions as defined by the Frank-Kamenetskii equation are met then thermal explosion

could take place.

In accord with eq 2 it is possible, by plotting $\log_e (r/T_1)$ as a function of the reciprocal of absolute temperature, to predict the critical ambient temperature which would need to be exceeded for thermal explosion to occur in a sample of a stated size and shape. As has been shown already, these calculations have been made on the basis of kinetic measurements made at approximately 400K. The compounds which followed a first order decomposition were observed to have melted prior to visible decomposition occurring and this has been put forward as a strong influence on their mode of decomposition, therefore it is likely that a small error in the prediction of critical radius could occur at temperatures below the melting point of these compounds where this mode of decomposition is not certain.

Table II gives the calculated induction times to the maximum rate of decomposition at 293 and 328K. At the temperature of 293K. the induction times are very long indeed but at 328K the times are considerably shorter ie for Jf-morpholinobenzene diazonium chlorozincate it is only 46 days. It is fairly certain that on the basis of these few results, the very long induction times at 293K would ensure that thermal explosion would be most unlikely to occur without some further external heat source. At the elevated temperature of 328K the induction times are shorter so as to amount to some risk in storage. This is especially so when it is considered that this is a maximum value and that the induction time would certainly be shorter due to some self-heating of the sample resulting from an acceleration in the rate of decomposition which could not be accounted for by the DSC.

The results of the critical radii calculated at 293 and 328K given in Table II together with induction time evidence, indicate that self-heating of any sample would be unlikely to take place at the lower of these two temperatures. However at 328K the critical radii for some compounds are relatively small in comparison with those at the lower temperature and it is conceivable that given sufficient time and the right size of sample self-heating leading to thermal explosion is possible. This is verified by experimental evidence which has shown that detectable decomposition was observed for these compounds at temperatures not much in excess of 328K.

At more elevated temperatures ie in excess of 400K it is clear that those compounds, which it has been shown decompose by an autocatalytic mechanism, have smaller critical radii than most of these other compounds and would be more sensitive to small intense sources of heat, which can be brought about by an impact on the sample and with the formation of a hot spot could lead to a thermal explosion. Work (18) on the impact sensitivities of these compounds has confirmed that in general they are more unstable to impact.

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TABLE I - Calorimetric determinations of enthalpy and kinetic parameters of decomposition

Diazonium salt	ΔH J g ⁻¹	Rate measurements				Time measurements Et kJ mol ⁻¹
		Er kJ.mol ⁻¹	factor	k _o s ⁻¹		
2, 5-diethoxy 4-morpholinobenzene diazonium chlorozincate (half salt)	617	101		11.3		—
2, 5-diethoxy 4-morpholinobenzene diazonium fluoborate	626	97.0		10.5		—
2, 5-diethoxy 4-p-tolylthiobenzene diazonium chlorozincate (half salt)	335	110	x	11.8	x	
4-morpholinobenzene diazonium chlorozincate (half salt)	613	160 ± 1.0 *		19.1 ± 1.0 *		145 ± 3 *
4-dimethylaminobenzene diazonium chlorozincate (half salt)	793	168 ± 14 *		20.4 ± 1.8 *		165 ± 4 *
4-dimethylaminobenzene diazonium fluoborate	653	172 ± 15		20.1 ± 2.0 *		175 ± 10 *
3-chloro 4-dibutylaminobenzene diazonium chlorozincate (half salt)	603	103		11.7		—
3 chloro 4-dibutylaminobenzene diazonium fluoborate	384	175		22.5		—
4-diethylaminobenzene diazonium chlorozincate (full salt)	591	150 ± 6 *		17.5 ± 0.7 *		169 ± 12 *
4-diethylaminobenzene diazonium fluoborate	620	104		11.3		
Temperature programmed decomposition x Rate measurements made when reaction rate decreasing * Isothermal decomposition Note: Error limits quoted are 95% confidence limits						

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TABLE II - Critical radii and induction time calculations at 293 and 328K

Diazonium salt	Calculated critical radii (m) for a spherical sample at temperatures:		Calculated induction times (s) at temperatures:	
	293K	328K	293K	328K
2, 5-diethoxy 4-morpholinobenzene diazonium chlorozincate (half salt)	0.46	0.06	—	—
2, 5-diethoxy 4-morpholinobenzene diazonium fluoborate	0.36	0.05	—	—
2, 5-diethoxy 4-p-tolythiobenzene diazonium chlorozincate (half salt)	2.06	0.20	—	—
4-morpholinobenzene diazonium chlorozincate (half salt)	5.80	0.29	3.64×10^9	4.41×10^6
4-dimethylaminobenzene diazonium chlorozincate (half salt)	6.16	0.33	2.24×10^{10}	1.60×10^7
4-dimethylaminobenzene diazonium fluoborate	17.7	0.71	5.19×10^{10}	2.42×10^7
3-chloro 4-dibutylaminobenzene diazonium chlorozincate (half salt)	0.32	0.03	—	—
3-chloro 4-dibutylaminobenzene diazonium fluoborate	2.79	0.07	—	—
4-diethylaminobenzene diazonium chlorozincate (full salt)	4.97	0.32	1.02×10^{11}	6.18×10^7
4-diethylaminobenzene diazonium fluoborate	0.62	0.07	—	—

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APPENDIX I - Measured values of density and thermal conductivity

Diazonium salt	Density: (kg m ⁻³)x10 ⁻³ at Room Temperature	Thermal conductivity (Jms ⁻¹ m ⁻² k ⁻¹) at Room Temperature
2, 5-diethoxy 4-morpholinobenzene diazonium chlorozincate (half salt)	0.41	2.9
2, 5-diethoxy 4-morpholinobenzene diazonium fluoborate	0.62	2.8
2, 5-diethoxy 4-p-tolythiobenzene diazonium chlorozincate (half salt)	0.40	2.9
4-morpholinobenzene diazonium chlorozincate (half salt)	0.59	2.9
4- dimethylaminobenzene diazonium chlorozincate (half salt)	0.55	3.2
4-dimethylaminobenzene diazonium	0.82	3.1
3-chloro 4-dibutylaminobenzene diazonium chlorozincate (half salt)	0.71	3.0
3-chloro 4-dibutylaminobenzene diazonium fluoborate	0.71	2.9
4-diethylaminobenzene diazonium chlorozincate (full salt)	0.54	2.7
4-diethylaminobenzene diazonium fluoborate	0.62	3.4

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