AN EPP STUDY OF THE THERMAL DECOMPOSITION
OF TNT/HMX MIXTURES

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When trinitrotoluene (TNT) is thermally decomposed, an observable radical signal is detected after several minutes at 240°C. Addition of hexamethylenbenzene (HMB) has been found to greatly reduce the temperature at which radicals may be observed (175°C or lower) and produce a radical signal which seems to be free of the polymeric species observed in the latter stages of TNT decomposition. Mixtures of TNT and HMB (.05 to .95 mole fraction of TNT) were thermally decomposed at 175°C to obtain a better identification of the radical species present in the early stages of TNT decomposition. Radical signals are observed which result from at least two species. The experimental spectra are correlated with simulated spectra of radicals derived from TNT and HMB. The relative rates of reaction and the form of the kinetic profile are dependent on the mole fraction of TNT.
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ABSTRACT

When trinitrotoluene (TNT) is thermally decomposed, an observable radical signal is detected after several minutes at 240° C. Addition of hexamethylbenzene (HMB) has been found to greatly reduce the temperature at which radicals may be observed (175° C or lower) and produce a radical signal which seems to be free of the polymeric species observed in the latter stages of TNT decomposition. Mixtures of TNT and HMB (.05 to .95 mole fraction of TNT) were thermally decomposed at 175° C to obtain a better identification of the radical species present in the early stages of TNT decomposition. Radical signals are observed which result from at least two species. The experimental spectra are correlated with simulated spectra of radicals derived from TNT and HMB. The relative rates of reaction and the form of the kinetic profile are dependent on the mole fraction of TNT.
This report describes work performed under FJSRL Work Unit 2303-F3-05 Chemical Structure/Bonding Relationships. C. Y. Kruijt was a temporary physical sciences technician at FJSRL, R. D. Murphy was a SCREE summer fellow working at FJSRL, W. R. Carper was an NRC working at FJSRL, S. R. Bosco was a staff member at FJSRL, and J. T. Swanson is a permanent staff member at FJSRL.
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The thermal decomposition of 2,4,6-trinitrotoluene (TNT) and related explosives is a research area which has been investigated for a number of years. The research has been directed towards two major concerns: the safe handling and storage of energetic materials and the systematic design of more stable and more energetic materials. TNT is known to decompose either thermally or photochemically.\(^1\)\(^2\) The decomposition products accelerate the rate of further decomposition. A number of other compounds, such as hexamethylbenzene (HMB) or tetralin, are also known to accelerate the decomposition of TNT. Addition of HMB will result in TNT radical signals in the EPR at temperatures of 175°C or lower, where no signal is observed for neat TNT. A potential problem is present when explosives are subjected to heat, such as during storage, or when carried aboard aircraft. Another problem occurs because modern ordnance, especially solid fuel motors, require the use of increasingly energetic materials such as HMX and RDX, which are considerably less stable, to shock, for example, than TNT. The first steps in decomposition appear to be the same as those in explosion or combustion. The deuterium isotope effect for HMX is the same, whether measured at relatively low temperatures by differential scanning calorimetry (DSC) or by recording relative burn rates of deuterated and undeuterated samples.\(^3\)\(^a\)\(^3\)\(^b\) Shock induced initiation can be accounted for in terms of thermal explosion theory using global reaction rates determined from slow thermal decomposition studies such as DSC.\(^3\)\(^b\)

Early EPR investigations of the thermal decomposition of TNT showed at least two radical species are present during the decomposition.\(^4\) The "early" radical possesses considerable fine structure and is believed to result from trapping of benzyl radical by a nitro group in TNT.\(^5\) The "late" radical shows only a broad singlet and is believed to be a polymeric species. The early radical initially grows in with a zero order rate. The spectrum at later times is dominated by the polymeric species growing in with a first order rate.

When HMB is mixed with TNT, a yellow solid, presumably a charge transfer complex, is obtained. The solid can be decomposed as low as 175°C or lower.
(just above the melting point of HMB) to produce at least two radical species possessing considerable fine structure. This paper presents the initial results from an investigation of these TNT/HMB mixtures, as a model of explosive binder interaction. The aims are to identify the species present early in the reaction mechanism, where one might reasonably hope to affect stabilization of the compound and to identify the properties of a binder which are likely to lead to sensitization of the resulting explosive/binder material.

II. EXPERIMENTAL

TNT in HMB at mole fractions of .05, .10, .20, .80, .90 and .95 were decomposed in a TE\textsubscript{102} cavity of a Varian E-109 EPR spectrometer operating in the X band. Samples were heated by a stream of nitrogen gas to 175°C. The temperature of the cavity was maintained to within ±.5°C as measured by a Doric Trendicator. Spectra were recorded on a MINC 11/23 with locally written software.

III. RESULTS AND DISCUSSION

Two major trends can be observed in the data. First, the kinetic plots of TNT in HMB (Figures 1 and 2) show the kinetics are not simple zero order. Rather, the shape of the kinetic plot is a function of the TNT/HMB ratio. Secondly, spectra (Figures 3 and 4), show at least two species are present whose relative concentration depends on the TNT/HMB ratio. The two results will be discussed in turn.

A. Kinetics

The kinetics were determined from the magnitude of the most prominent peak in the EPR spectrum. The actual mechanism for the decomposition of TNT has not been established. The main features of the mechanism involve formation of benzyl radical, coupling of this radical with a nitro group on the aromatic ring, and further reaction of this species to form polymeric materials. The purpose of doing the kinetic fit is to determine the intensity of the radical species, R, which produces the predominant lines in the ESR spectrum, as a function of time. Since the mechanism is not known, we have chosen to fit the
fig 1. Decomposition of .05 Mole Fraction TNT in HMB

fig 2. Decomposition of .95 Mole Fraction TNT in HMB
fig 3. Spectrum of Radical Intermediate: .05 Mole Fraction TNT

fig 4. Spectrum of Radical Intermediate: .95 Mole Fraction TNT
kinetics with a production term \( Q(t) \), minus the rate of loss of \( R \), assumed to be \( k[R] \) (Equation 1).

\[
\frac{d[R]}{dt} = Q(t) - k[R] \tag{1}
\]

The simplified partial mechanism is shown in scheme 1.

\[
\begin{align*}
\text{TNT} & \rightarrow B \\
B & \rightarrow R \\
R & \xrightarrow{k} P
\end{align*}
\]

Scheme 1. Decomposition of TNT in HMB

TNT is decomposed through an indeterminant number of steps to a radical \( R \). In theory, radical \( R^* \) could be formed directly from TNT. It may however also be formed later in the reaction from some intermediate species \( B \). Scheme 1 shows this most general case. The observed radical then reacts to form the product polymer \( P \) with rate constant \( k \). Several different production terms were considered for radical \( R \). As a preliminary investigation production terms were chosen which made chemical sense and for which the rate equation had a closed solution. These terms are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Possible Radical Production terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ( Q(t) = \text{constant} )</td>
</tr>
<tr>
<td>(b) ( Q(t) = N_0 e^{-bt} )</td>
</tr>
<tr>
<td>(c) ( Q(t) = N_0 e^{-bt} + C )</td>
</tr>
<tr>
<td>(d) ( Q(t) = c[1 - e^{-bt}] + A[e^{-dt} - e^{-bt}] )</td>
</tr>
</tbody>
</table>

Equation (a) assumes a steady state production, for example first order production directly from TNT where the conversion is low. Equation (b) assumes the rate of radical production drops off with time, for example, first order production from TNT where conversion is high. In this case \( b \) would be the rate constant for the loss of TNT. Equation (c) assumes the rate of production falls off to a steady state value, rather than to zero. Equation (d) assumes the rate is initially zero, rises to a maximum, and then falls to
fig 3. Fit of Decomposition of .05 Mole Fraction TNT

fig 4. Fit of Decomposition of .06 Mole Fraction TNT
a constant value. This type of rate behavior could arise only if radical R is formed from some earlier radical (B).

For low mole fraction of TNT, setting \( Q(t) = \text{constant} \) is a sufficiently good fit for the kinetics. However, \( Q(t) = N_0 e^{-bt} + C \) is necessary to fit the kinetics of the high mole fraction of TNT. Making the assumption that the rate law remains the same as the mole fraction of TNT in the sample is changed, one can fit all the data using production term (c) and setting the rate constants b and k equal. Thus, the rate of production and loss of radical R will be about equal and steady-state conditions (as observed) will apply. The fits for two mole fractions of TNT are shown in Figures 5 and 6. The rate constants derived and the fit to various overall rate equations are shown in Table 2.

### Table 2. Rate Constants for TNT/HMB Decomposition.

<table>
<thead>
<tr>
<th>Mole Fraction TNT</th>
<th>Rate Constant</th>
<th>( k/[\text{TNT}]^2[\text{HMB}] )</th>
<th>( k/[\text{TNT}][\text{HMB}] )</th>
<th>( k/[\text{TNT}][\text{HMB}]^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.05</td>
<td>.0065</td>
<td>2.74</td>
<td>.137</td>
<td>.144</td>
</tr>
<tr>
<td>.10</td>
<td>.01</td>
<td>1.11</td>
<td>.111</td>
<td>.123</td>
</tr>
<tr>
<td>.20</td>
<td>.017</td>
<td>5.35</td>
<td>.107</td>
<td>.133</td>
</tr>
<tr>
<td>.80</td>
<td>.01</td>
<td>2.34</td>
<td>1.872</td>
<td>9.38</td>
</tr>
<tr>
<td>.90</td>
<td>.185</td>
<td>2.28</td>
<td>2.052</td>
<td>20.56</td>
</tr>
<tr>
<td>.95</td>
<td>.15</td>
<td>3.32</td>
<td>3.154</td>
<td>63.16</td>
</tr>
</tbody>
</table>

The results seem to indicate that the rate is not simply first order in TNT and HMB i.e. rate = \( k [\text{TNT}][\text{HMB}] \). The best fit assuming a single mechanism is rate = \( k [\text{TNT}]^2[\text{HMB}] \). This might imply the reaction involves a charge transfer complex of TNT and HMB which then reacts with TNT to start the reaction. As the charge transfer complex is likely to be more reactive, the reaction should occur at lower temperature. The data indicates the mechanism could also involve two TNTs at high mole fraction of TNT and two HMBs at high mole fraction of HMB. This possibility will be discussed in more detail in the section on the analysis of the spectra.
Fig 7. Fit of decomposition of .90 mole fraction TNT

Fig 8. Decomposition of .95 mole fraction TNT
We have just begun trying to fit the kinetics to production term (d). Close examination of the high mole fraction TNT curves show that the slope at the beginning of the reaction has the opposite curvature to that given by fit (c). Using term (d) corrects the problem (Figure 7). Because of the large number of parameters, determining a best fit is somewhat difficult. This fit supports the postulate that the first radical seen in the EPR is not the first formed radical. Rather an earlier radical(s) is formed which reacts to form the more stable radical observed by EPR.

One of the primary problems involved in these kinetics is the presumed sensitivity of the kinetics to small impurities. The radical concentrations of $10^{-6}$ M can be observed by EPR and so small impurities can result in large rate changes. However, the shapes of the kinetic curves are consistent for a particular mole fraction of TNT. One reason the radical signal may not be falling to zero is contamination due to formation of the polymeric species. Evidence for this comes from some runs where the polymer signal began appearing at the end of the run (Figure 8).

B. Spectra

The spectra derived from the TNT/HMB mixtures clearly indicate a number of different species present. The asymmetry of the overall spectra tends to indicate two or more overlapping species with slightly different g values. A comparison of the spectra obtained at different mole fractions of TNT provides evidence for two species whose relative abundance depends on the mole fraction of TNT. One possibility is that one of the radicals is produced from one TNT and one HMB, the other from two TNTs. Several types of evidence support this postulate. First, the relative amounts of the species change with mole fraction. With just a trace of HMB, the spectrum resembles pure TNT, but the reaction proceeds more rapidly. The total intensity of the spectrum is much higher in the mixtures with high mole fraction of TNT, indicating it is important in forming the radical. Also, each spectrum contains a five line pattern with coupling of 11 G. This pattern almost certainly requires a nitrogen coupling. The overall intensity pattern is best fit by one nitrogen and two hydrogens, each with 11 G coupling constants.
Figure 9. Possible intermediates in TNT/HMB Decomposition
The spectra themselves are difficult to fit and several possibilities have been considered. The radical predominant when TNT is in large excess over HMB consists of a five line pattern with a coupling of 11 G. Within this pattern is some further hyperfine splitting into five lines with a coupling constant of 2.6 G. One possible interpretation of this pattern is one nitrogen and two hydrogens each with a coupling constant of 11 G and four hydrogens with a coupling constant of 2.6 G. A possible structure is shown in Figure 9a.

The para nitrobenzyl radical, however, has been shown to be difficult to produce. The second radical, in about equal concentrations with the first at high HMB mole fractions, also shows a five line pattern with coupling of about 11 G. No further fine structure can be identified. Because of this pattern, this radical also appears to result from TNT, perhaps also having 1 N and two large H coupling constants. The benzyl type radical expected from HMB would only show two lines and may be buried under the spectra of other species. Simulation of the spectra using the above coupling constants (Figure 10) shows the correct general trend in peak heights and shapes, but insufficient splitting.

Another possibility is that the species present are very similar to the species believed present in neat TNT. For example, the two species might be of the type shown in Figure 9b, where the benzyl moiety could be due either to TNT or HMB. The simulation for this species is shown in Figure 11. The best fit found so far is for one species obtained from $1N = 11 \text{ G}$, $2H = 11 \text{ G}$, $2H = 2.7 \text{ G}$, $1N = 11 \text{ G}$, $2H = 11 \text{ G}$, and $2H = 2.7 \text{ G}$. Nitrobenzene radical anion has a nitrogen coupling constant of $a_N = 10.3 \text{ G}$ and for the hydrogens $a_{O,H} = 3.5 \text{ G}$, $c_{CH} = 1.1 \text{ G}$, and $a_{CH2} = 3.967$. Phenyl benzyl nitroxide has $a_N = 9.5 \text{ G}$, $a_{O,P} = 2.6 \text{ G}$, and $a_{CH2} = 5.26 \text{ G}$. The first of these species is the same as that postulated in the decomposition of neat TNT. It is difficult to assign a structure for the second.

**IV. CONCLUSION**

The results of these preliminary measurements indicated several trends. First, the first observed radical does not appear to be the first radical formed, based on the kinetics. Secondly, while HMB and TNT both seem to be
important in the initiation of the mechanism, the EPR spectra indicate TNT is a constituent of all the radicals observed. Thus, TNT appears crucial in the propagation of the reaction. One possibility is that the TNT/HMS charge transfer complex initiates the formation of radicals, which are then consumed to form EPR observable species through propagation steps with TNT. These initial studies suggest the need for more detailed analysis, which will be accomplished as computational facilities become available.

These results also show that in propellants or explosives which are mixtures of several components, thermal decomposition and degradation may become a major problem. Addition of additives to TNT such as hydroxide or quinone have been shown to result in decreased thermal stability and increased sensitivity to shock. Understanding the detailed mechanism of these processes will hopefully allow the facets of the chemical structure which lead to degradation to be designed out, without affecting the energetic performance of the compound.
V. REFERENCES

   


   


