50
8-30-74
MLM-2113

DN-916
MLM-2113

PETN Stability and Compatibility

D. M. Colman and R. N. Rogers

July 15, 1974

AEC Research and Development Report

MOUND LABORATORY

Miamisburg, Ohio
operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company
for the

U. S. ATOMIC ENERGY COMMISSION

U. S. Government Contract No. AT-33-1-GEN-53

Monsanto

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PETN Stability and Compatibility

D. M. Colman and R. N. Rogers

Issued: July 15, 1974

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PRINTED IN THE UNITED STATES OF AMERICA

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$4.00 Microfiche \$1.45

MONSANTO RESEARCH CORPORATION

A Subsidiary of Monsanto Company

MOUND LABORATORY

Miamisburg, Ohio 45342

operated for

UNITED STATES ATOMIC ENERGY COMMISSION

U. S. Government Contract No. AT-33-1-GEN-53

MA 3

ABSTRACT

The decomposition kinetics of pentaerythritol tetranitrate (PETN) alone and in admixture with other materials has been studied using a differential scanning calorimeter. Quantitative rate and reaction order(s), as a function of composition, were obtained.

It is possible to calculate the reaction order of the decomposition from the data as well as the pre-exponential and energy of decomposition for the Arrhenius rate equation, $k = Ae^{-E/RT}$ or $k = Ze^{-E/RT}$. Changes in the foregoing parameters, singly or in combination, tend to indicate the degree of compatibility of the materials undergoing the test.

In order to postulate a reaction mechanism(s), one must be able to identify the reaction products. An attempt to identify reaction products was begun by using a pyrolysis - thin layer chromatographic procedure. Though the evidence obtained was from a dynamic mode of operation, the experiments could have been done isothermally.

An approximate temperature for the presence of formaldehyde was found to be 398°K, which is below the melting point of PETN. When the test was made using EXON 461 alone, chlorine was found at approximately 433°K.

It would seem that the combination of these techniques could provide a useful method in elucidating compatibility information. Because of the small size of the samples used, the procedures would be safe and could be developed into a practical routine method.

PETN STABILITY AND COMPATIBILITY

D. M. Colman and R. N. Rogers*

Recent observations made at Mound Laboratory in conjunction with a study on the corrosion of gold in contact with pentaerythritol tetranitrate (PETN) have made it important to obtain a complete understanding of the kinetics and mechanism of decomposition of PETN and the effects of materials in contact with PETN.

It was also thought that the PETN system would be excellent to use to check some hypotheses on the quantitative measurement of compatibility, because many materials have been found to be incompatible with PETN.¹ Measurements of rate constants and reaction order as a function of composition as a second material is added should allow us to observe, measure, and describe the type of compatibility problem encountered.

In order to observe changes in the decomposition kinetics of PETN, it is necessary to understand the unperturbed reaction rather well. It has generally been recognized that the decomposition of PETN is autocatalytic. Robertson² noted that there was "---a very nearly constant rate of gas evolution for about the first half of the decomposition, after which this rate diminished in accordance with the unimolecular equation." He used the "---slope of the initial straight portion of the curve---" for his calculation of the kinetics constants, obtaining the values $E = 47 \pm 1.5$ kcal/mole and $Z = 6.31 \times 10^{19} \text{ sec}^{-1}$. Andreev and Kaidymov³ reported that the absolute rate increased up to about 30% decomposition. They fitted the entire curve to obtain values as follows: $E = 39$ kcal/mole, $Z = 3.98 \times 10^{15} \text{ sec}^{-1}$. A DSC rate curve is shown in Figure 1, and the undecomposed fraction $(1 - x)$ is shown in the graph. It can be seen that the rate increases up to 30% decomposition, a feature that can be seen more clearly in lower-temperature runs.

*Mr. Rogers is a member of the WX-2 Group, Weapons Engineering Division, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

A first-order plot and an order plot for the run shown in Figure 1 are shown in Figure 2. The early part of the decomposition is almost exactly first order, and a very consistent linear first-order plot is obtained for calculation of the rate constant. The entire reaction more closely approaches first order at lower temperatures, as shown in Figure 3.

When the early first-order part of the reaction is used for the calculation of the kinetics constants, the result is as shown in Figure 4. ($E = 46.5$ kcal/mole, $Z = 2.36 \times 10^{19}$ sec⁻¹). This is an excellent check with Robertson's results for the same reaction regime. This series of runs was also used to compare results achieved with the DSC-1B with those from a new DSC-2. It can be seen that there is no significant difference between the two sets of data; however, the noise level in DSC-2 rate curves is extremely low, making those curves easy to measure. Robertson had noted that rates did not change over a range of gas pressures from 5 to 76 cm; therefore, we compared DSC runs at two different degrees of confinement: cells perforated with a needle (0.1-mm perforation) and cells perforated with a laser beam (12- to 15- μ m perforation). No significant difference could be seen between the sets of data.

When the late part of the reaction is used for the calculation of the kinetics constants, the results are as shown in Figure 5 ($E = 33.9$ kcal/mole, $Z = 4.68 \times 10^{13}$ sec⁻¹). Again, there is no significant difference observed as a function of instrument used or confinement. A comparison between the early and late data proves that the decomposition is indeed autocatalytic. Robertson², Andreev and Kaidymov³ reported that NO₂ was produced early in the reaction and disappeared later; however, the lack of effect of fill-gas pressure and confinement seems to indicate that the main secondary reactant is generated in the liquid phase.

A material that affects the mechanism of the decomposition reaction will cause a change in the rate constant of the process at any temperature. The change in rate can be the result of a change in activation energy, pre-exponential, or both, and higher-order reactions can appear as a function of mixture composition. Insoluble materials with active surfaces can contribute zero-order processes to an overall decomposition. Examples of all the types of reactions have been observed with the DSC, but there has never been an opportunity to study the systems in detail.

In application, PETN is often used in contact with PBX 9407, a mixture of cyclotrimethylenetrinitramine (RDX) and Exon 461, a Firestone Plastic Co. polymer containing chlorine; therefore, the

FIGURE 1 - Differential scanning calorimeter (DSC) rate curve from 0.706-mg sample of PETN at 490°K, run in a cell with 0.022-ml capacity and a single 0.1-mm diameter perforation. The residual fraction $(1-x)$ is shown at each indicated position.

FIGURE 2 - First-order plot (left) and order plot (right) from decomposition curve shown above in Figure 1.

FIGURE 3 - Order plot for 460°K decomposition of PETN.

FIGURE 4 - Arrhenius plot of early first-order data (21 points) from PETN decompositions; least-squares results are $E = 46.5$ kcal/mole and $Z = 2.36 \times 10^{19} \text{ sec}^{-1}$. Robertson, Andreev and Kaidymov least-squares lines are shown for comparison. Numbered points indicate the following conditions: (1) DSC-2 with 0.1-mm perforation in cell, (2) DSC-1B with 0.1-mm perforation in cell, (3) DSC-2 with 12-15 μm perforation in cell, and (4) DSC-1B with 12-15 μm perforation in cell.

FIGURE 5 - Arrhenius plot of late rate data from PETN decompositions (22 points). Least-squares line indicates $E = 33.9$ kcal/mole and $Z = 4.68 \times 10^{13} \text{ sec}^{-1}$.

first compatibility tests were run with RDX and Exon. Figure 6 shows the Arrhenius plot obtained from mixtures of PETN with 5% RDX, superimposed on the Arrhenius plot of the early PETN data. The RDX degrades the PETN to a barely detectable extent. The order plot of Figure 7 shows that the process is still first order. Studies at other compositions should be made to understand the interaction, but the system certainly is not hazardous.

The Arrhenius plot for the PETN/5% Exon system is shown in Figure 8; there is a definite increase in rate. Figure 9 shows that there is an accompanying increase in reaction order. Other compositions will be studied as time allows.

It is evident that differential scanning calorimeter (DSC) techniques now exist that could provide useful quantitative compatibility information safely on very small samples. It is hoped that these methods can be developed into practical routine methods in the near future.

The data and conclusions drawn allow the determination of the reaction order and the calculation of the Arrhenius constants E and Z (or A). Although invaluable, this information does not allow the postulation of one or more reaction mechanisms. The reaction products as well must be known in order to elucidate the decomposition reaction mechanisms.

A start in this direction was made using the pyrolysis thin layer chromatographic procedure of Rogers ⁴. The experimental parameters were as follows:

sample weight	approximately 50 mg
nitrogen gas flow	25 ml/min
linear temperature programming rate	11°/min
temperature range	ambient to 523°K (250°C)

Gelman SA sheets were drawn through a 1.0 wt% aqueous solution of AgNO₃, then hung to dry in a dark hood.

Preliminary experiments had shown that silver precipitated immediately when the impregnated sheet was exposed to formaldehyde. This was not true for other aldehydes. When the impregnated sheet was exposed to Cl⁻ or Cl₂, eluted with water in the ascending mode, dried, and finally exposed to uv light, a gray to black spot formed where the reaction took place.

FIGURE 6 - Arrhenius plot of PETN/5% RDX data, superimposed on line for early PETN data.

FIGURE 7 - Order plot of 480°K data from a PETN/5% RDX decomposition.

FIGURE 8 - Arrhenius plot of PETN/5% Exon 461 data, superimposed on line for early PETN data.

FIGURE 9 - Order plot of 475°K data from a PETN/5% Exon 461 decomposition.

Pyrolysis of PETN indicated that formaldehyde was forming at approximately 398°K. No attempt was made, at this time, to identify other decomposition products. It is interesting to note that decomposition is taking place below the PETN melting point 414°K. Yates⁵ has identified HCN at temperatures below 414°K. There may be two types of PETN decomposition mechanisms, one that takes place at low temperature (below the melting point), and the other a high temperature decomposition (above the melting point).

Pyrolysis of Exon indicated that Cl is a decomposition product appearing at approximately 433°K. When the mixture of PETN/Exon (95/5) was run, the formaldehyde appeared at 398°K and the Cl appeared at 433°K. One may conclude that the Exon and PETN could be compatible in this mixture and in this temperature range.

It should be noted that both types of experiments were conducted in an inert atmosphere (nitrogen). The question arises as to whether the same results would be obtained if the experiments were made in the presence of oxygen (air).

Though the pyrolysis experiments were done in a dynamic mode, there is no reason that they could not have been done in the isothermal mode. In the isothermal mode, one may be able to determine the lowest temperature and shortest time that a particular decomposition product can appear.

Utilizing the information obtained from both types of experiments will no doubt lead to a more complete solution of compatibility studies.

REFERENCES

1. R. N. Rogers and E. D. Morris, Jr., Anal. Chem., 38, 412 (1966).
2. A. J. B. Robertson, J. Soc. Chem. Ind. (London), 67, 221 (1948).
3. K. K. Andreev and B. I. Kaidymov, Zh. Fiz. Khim., 35, 1324 (1961).
4. R. N. Rogers, Anal. Chem., 39, 730 (1967).
5. W. G. Yates, Mound Laboratory, private communication.

P. F. Carpenter, Editor