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THE INFLUENCE OF METALS ON THE THERMAL DECOMPOSITION
OF s-TRIAMINOTRINITROBENZENE (TATB)

by

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ABSTRACT

Although s-triaminotrinitrobenzene (TATB) possesses unusually high thermal stability for an organic explosive, the rate of gas evolution at elevated temperatures appears to be increased markedly by the presence of copper, iron, or brass. Aluminum in the same experimental environment produces little or no effect on the gas evolution rate. This paper presents the results of various experiments in which attempts were made to evaluate the magnitude of the effects and to elucidate the mechanism of the thermal degradation of TATB both in the pure state and in the presence of the aforementioned metals.

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I. INTRODUCTION

TATB and TATB formulations have been under study at the Los Alamos Scientific Laboratory (LASL) for a number of years. Interest in this compound as a secondary explosive stems mainly from its relatively high thermal stability and its insensitivity to initiation by friction and impact. Table I summarizes some of the properties of TATB that make it attractive as an explosive, and Figure 1 displays schematically the structure of the molecule. The x-ray spectrum of crystalline TATB¹ reveals that the C-C bond orders are approximately 1.2 and the amine C-N and N-O bond orders are nearly 1.5. It is also evident that the molecule is nearly planar and that an extensive system of hydrogen bonds exists. This latter feature of the crystal structure undoubtedly contributes to the thermal stability of the solid and tends to make the material insoluble in most common solvents. Although it is not as energetic an explosive as the more widely used HMX and RDX formulations, it is sufficiently powerful for certain applications where the size of the charge is not severely restricted and the stability characteristics of TATB are desirable.

II. BACKGROUND

We are aware of very little published work on the thermal decomposition of TATB. The United States Naval Ordnance Laboratory (NOL) first became interested in its potential as a heat-resistant explosive in the 1950's and reported briefly on its properties.² Several laboratories have investigated specific properties of the compound in more detail, e.g., molecular structure,^{3,4} vapor pressure,⁵ and shock Hugoniot.⁶ Serious evaluation of TATB and its formulations began in our laboratory in 1965 and has continued to this date.

Our first estimates of the thermal stability of TATB were obtained in short-term, high-temperature tests such as a 260°C vacuum stability test, differential scanning calorimetry (DSC), and Henkin time-to-explosion tests⁷ at even higher temperatures. Although kinetics constants determined by the

DSC method correctly predicted the critical temperature determined in the Henkin test, extreme environmental requirements imposed by several proposed applications of TATB explosives prompted us to initiate long-term stability tests at the temperatures of interest. It was during these experiments that a striking incompatibility between brass and TATB was observed, initiating further studies into the thermal decomposition mechanism of this compound.

III. EXPERIMENTAL

The TATB used in the work reported herein was prepared at LASL by an improved process, based on the NOL synthesis,² that resulted in a higher purity product. The purity level was greater than 99%, the major impurity being NH_4Cl .

Long-term gas-evolution studies were performed on samples of powder, pressed pellets, and Henkin cells sealed in Pyrex ampoules filled with a cover gas of dry air or argon. The sealed ampoules were stored in temperature-controlled ovens at 177 or 204°C for various lengths of time. After removal from the ovens, the ampoules were opened on a CEC 21-103 mass spectrometer inlet system where gas volumes were measured and mass spectra of the gases obtained. In several instances the solid residue remaining in the ampoules was removed, weighed, and analyzed by several techniques, including elemental analysis, x-ray diffraction, and mass spectrometry.

The sealed-ampoule studies necessarily produced results that reflected processes occurring in a closed environment, including back reactions of gaseous products with the solid and product reactions in the gas phase. In the hope of elucidating primary reaction mechanisms, several experimental techniques were employed that rapidly removed the gaseous products from the reaction zone, namely thermal gravimetric analysis (duPont Model 950 TGA), pyrolysis, and pyrolysis/TOFMS (Perkin-Elmer Pyrolysis Accessory/Bendix MA-2 time-of-flight mass spectrometer). In all these methods, helium was used as the carrier gas with flow rates ranging from 0.2 to 0.8 cm^3/s . A simple flow-splitter was incorporated into the heated effluent line of the pyrolysis accessory to reduce the flow into the mass spectrometer to an acceptable level (~ 2% of the total

effluent). Pure TATB samples and TATB/metal mixtures were contained either in open platinum boats or sealed aluminum DSC cells for the TGA and pyrolysis studies. In several instances, small perforations were made in the sealed DSC cells, and various metal powders were layered over the TATB in the open boats. The techniques of data collection and reduction were more or less conventional for these experimental methods and will not be detailed here.

IV. RESULTS AND DISCUSSION

Table II contains typical weight-loss data for TATB stored at 204°C for 14 days in various containers. Mass spectrometric analyses of the evolved gases in the sealed-container experiments showed that the major gaseous product was CO_2 , constituting more than 50% of the mixture. Lesser amounts of N_2 , CO, and H_2O also were present. In those samples where extensive decomposition had occurred, a white residue formed on the inner surface of the glass ampoule upon removal from the oven. This substance was identified by x-ray analysis as ammonium bicarbonate and represented about 20% of the total weight loss. Brass Henkin cells containing TATB and sealed inside Pyrex ampoules developed a bluish deposit on the cell surface after storage at 204°C for one week. The bluish deposit was identified by x-ray analysis as $(\text{NH}_3)_4\text{CuCO}_3$. Figures 2 and 3 graphically illustrate the dramatic difference in rates of gas evolution from TATB samples stored in brass Henkin cells compared with those stored in aluminum cells or as unconfined powder. Note the difference in the magnitude of the evolved-gas numbers at the two temperatures. This information is presented to illustrate the magnitude of the effect observed with these particular experimental conditions.

The point of interest in these data is the pronounced difference between the rates of gas evolution from the two different Henkin-cell materials. The TATB in aluminum cells decomposed at a rate comparable with that observed with TATB powder sealed in Pyrex ampoules. The TATB sealed in brass cells decomposed quite rapidly. These results led us to investigate more thoroughly the TATB decomposition reaction.

Because of the complexity of the reactions in the sealed containers, extensive use was made of the flow techniques described previously in the hope of obtaining some information about the primary decomposition products and the reaction mechanism. Since the sublimation rate of TATB is moderately high at the temperatures that make the use of flow techniques practical, quantitation of the thermal decomposition reaction was difficult. However, it was felt that comparative observations were meaningful and useful in attempting to unravel the mechanisms of the systems studied.

Differential thermal analysis (DTA) curves for Cu/TATB, Fe/TATB, and Zn/TATB mixtures, obtained at a heating rate of 0.66°C/s (40°C/min), showed an exothermic reaction occurring at temperatures 50 to 75°C lower than the major decomposition exotherm in pure TATB at 350°C . Aluminum appeared to have little if any effect on the DTA curve for TATB. It should be pointed out that the sample mixtures were simple physical mixes of the metal and TATB powders in a weight ratio of about 20/1 TATB/metal. No pretreatment of the metal powders was done and the particle surfaces of the more active metals were certainly coated with oxide to varying degrees. A reproduction of several DTA curves is shown in Figure 4.

Thermal gravimetry data obtained on several Cu/TATB mixtures indicated that the rate of decomposition of TATB was markedly dependent upon the amount of Cu powder in the mixtures. In mixtures containing a large excess of Cu, the reaction proceeded very rapidly (at the temperatures studied) to completion, consuming nearly all the TATB. When only a small amount of Cu was present, the decomposition proceeded rapidly for a short time, then it continued at a rate comparable with that of pure TATB. In most instances some unreacted TATB remained after the reaction ceased. Examples of these results are shown in Fig. 5. These data imply that a large active surface of Cu catalyzes or accelerates the decomposition of TATB, and as the reaction proceeds the surface of the Cu becomes coated or otherwise poisoned by reaction products.

The TATB/metal mixtures were subsequently studied using the pyrolysis/-TOFMS equipment. Both isothermal and programmed temperature pyrolyses were

performed, and the effluent gases were analyzed after they were swept from the reaction zone by the helium carrier gas.

The temperature of the interface between the pyrolyzer and mass spectrometer was maintained at about 150°C, and the time between reaction in the pyrolyzer and mass analysis of the evolved gases was less than 1 second. The results obtained on samples of pure TATB and TATB mixed with silica and aluminum powder indicated that thermal decomposition at temperatures below 450°C produced CO₂, NO, HCN, C₂N₂, and a mass 43 species, believed to be an HNCO isomer. A solid organic residue remained after every run. Samples of TATB mixed with Cu and Fe powder gave larger amounts of CO₂ and very little NO or HCN. In several runs, large amounts of the metal powder were layered over a small sample of TATB. This resulted in a larger amount of evolved gas per gram of TATB, but no NO or HCN was produced with the active metals. Less residue was obtained in these latter pyrolyses. Table III summarizes the results of the evolved-gas analyses in both the flow and sealed-ampoule experiments. These results imply that a TATB vapor/metal reaction is occurring. Attempts were made in several instances to analyze the product residue for C,H,N, and O content, but these analyses were somewhat difficult because of the refractory nature of the material. However, it appeared that the residual organic matter was lower in O content in those experiments where TATB was mixed with Cu and Fe than when pyrolyzed alone or with silica or Al.

We have attempted to formulate a reaction mechanism from the limited experimental information collected to this point. Two possible reaction schemes are depicted in the next two figures. Figure 6 shows a process in which a molecule of H₂O is eliminated from a TATB molecule, resulting in a substituted benzofurazan compound which could further decompose to give reactive cyanogen oxide and other products. Supporting this scheme, a small peak at mass 68 (C₂N₂O ?) was observed in the mass spectrum of the evolved gases in several flow experiments with pure TATB. Also, a similar benzofurazan derivative has been obtained in the thermal decomposition of diamino-trinitrobenzene (DATB).⁸ A reaction between two molecules of TATB with the

elimination of H_2O can also be postulated. The condensation product could then proceed to decompose in a similar fashion as above.

Figure 7 presents a second scheme, which seems to apply more specifically to the reaction with metals. In this case, an oxidizable substance, the metal or TATB itself, reacts with TATB to form an oxide and an unstable 1,2-imid-oxime intermediate that decomposes rapidly to give the products shown. In a closed system, these materials could further react rapidly to give the observed stable end products, CO_2 , NH_3 , and N_2 .

V. CONCLUSION

We have observed a marked acceleration in the rate of thermal decomposition of TATB at elevated temperatures in the presence of copper and iron by several experimental methods. Aluminum, under the same conditions, appears to have little or no effect. The results at this point indicate that a reaction occurs between gaseous components (TATB vapor and/or decomposition products) and the metals. A specific reaction mechanism explaining the catalytic effect of certain metals has not yet been formulated. However, copper and iron are relatively strong reducing substances, and we believe that similar metals would also accelerate the TATB decomposition. Information such as that obtained in this study can be of practical significance when considering TATB for a particular application where exposure to active metals is possible.

VI. ACKNOWLEDGMENTS

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TABLE I

PROPERTIES OF TATB

- a) It has a crystal density of 1.938 g/cm^3 , which is exceptionally high for an organic explosive.
- b) It is very insensitive to impact and friction, as shown by drop-weight impact and skid tests.
- c) It possesses excellent thermal stability. In the DTA apparatus, exothermal decomposition begins at about 330°C ; in the vacuum stability test at 260°C , it evolves 0.6 ml of gas/g of sample/h.
- d) Its explosive power is superior to that of other heat-resistant explosives. At crystal density, its detonation pressure and velocity are calculated to be 313 kbar and 7970 m/s, respectively.
- e) It is essentially insoluble in all common solvents and chemically is quite inert.
- f) A network of intermolecular hydrogen bonds gives the crystals a graphite-like structure, and the crystals exhibit many of the properties to be expected of such a structure.

TABLE II

PERCENT WEIGHT LOSS OF TATB AFTER 14 DAYS AT 204°C

<u>Container</u>	<u>Weight Loss (%)</u>
Pyrex Ampoule	1 ³
Al Jenkin Cell	2
Brass Henkin Cell	50
Vacuum Stability (200°C)	0.6 ³
DSC Predicted	1.4

³Calculated from measured gas volumes and assuming
a molecular weight for the gas of 38.

TABLE III

NATB GASEOUS DECOMPOSITION PRODUCTS

(Inert Atmosphere)

	<u>Additive</u>	<u>Products</u> [*]
Flow Experiments	None	CO ₂ , C ₂ N ₂ , NO, CHNO, HCN
(280-450°C)	SiO ₂	Same
	Al	Same
	Cu	CO ₂ , CHNO
	Fe	CO ₂ , C ₂ N ₂
Static Experiments	None	CO ₂ , N ₂ , CO, NH ₃ , H ₂ O
(177-204°C)	Al (Henkin Cell)	" " " H ₂ O, H ₂
	Cu	" " " NH ₃ , H ₂ O
	Brass	" " " " "

* Listed in order of decreasing relative abundance as estimated from mass spectral data.

DIAGRAM OF THE TATB MOLECULE IN A CRYSTAL

Figure 1

TOTAL EVOLVED GAS FROM SEALED-
AMPOULE SURVEILLANCE OF TATB
CONTAINED IN HENKIN CELLS AT 177° C

Figure 2

TOTAL EVOLVED GAS FROM SEALED-
AMPOULE SURVEILLANCE OF TATB
CONTAINED IN HENKIN CELLS AT 204°C

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7