MASTER

MHSMP-76-30D
Revision 1

PRODUCTION AND IDENTIFICATION OF
TATB-RELATED SPECIES

C. S. MacDougall
B. J. Jacobs

QUALITY DIVISION

APRIL - JUNE 1976

Normal Process Development
Endeavor No. 106

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant

P. O. BOX 30020
AMARILLO, TEXAS 79177
806.335-1581

operated for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
under
U. S. GOVERNMENT Contract EY 76 C 04 0482

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor 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.

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.

Fig. 2. Thin Layer Chromatograms of TATB Impurities

PRODUCTION AND IDENTIFICATION OF TATB-RELATED SPECIES

C. S. MacDougall
B. J. Jacobs

QUALITY DIVISION

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, 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.

April - June 1976
Endeavor No. 106

eb
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

Two major impurities in TATB were synthesized and identified by IR spectroscopy and thin-layer chromatography for use as analytical standards in TATB analysis.

INTRODUCTION

A large amount of effort has been expended in chemical characterization of TATB. A major portion of this effort has been directed towards assay of the TATB. This particular report concerns the synthesis and identification of several species which are impurities in the TATB. Work by W. T. Quinlin(1), et.al., shows the following sequence of reactions.

Since species 5 and 6 (above) are the major impurities in the TATB, it was necessary to synthesize these materials for use as standards in any analytical development scheme for the TATB. The tetrachlorodinitrobenzene (T_4CDNB) and trichlorodinitrobenzene (TCDNB) were provided by T. Quinlin and C. L. Schaffer of Development Division. These materials were then aminated and the reaction products were recovered and identified by IR spectrophotometry and thin-layer chromatography.

EXPERIMENTAL

APPARATUS

All IR spectra were taken using a Perkin-Elmer Model 521 Grating Spectrophotometer. Chloride measurement were performed by converting the organic chloride to ionic chloride by combustion in a Paar bomb, followed

by a potentiometric titration using a Beckman expandomatic pH meter. The electrodes were the Orion 94-17A chloride specific ion electrode and the Orion 90-01-00 single junction reference. Melting points were taken with a Mettler FP-5 thermometric analyzer. Thin-layer chromatographs were produced using Silica-G-Zn plate.

SAMPLE PREPARATION

A 75 mg portion of T₄CDNB was dissolved in 20 ml toluene. This solution sealed in a high pressure stainless steel reaction vessel equipped with a metal sealed valve capable of withstanding temperatures up to 200 C. The vessel was evacuated, filled with NH₃, and then evacuated and refilled with NH₃ to a pressure of 95 psi. The amination proceeded for 48 hours at a temperature of 50 C. After removal of the vessel from the oven, the sample was allowed to cool to room temperature, and the residual NH₃ was bled off. The reaction product was then removed from the vessel and the toluene evaporated. This residue was then redissolved in fresh toluene and recrystallized from toluene.

Next, a 75 mg portion of TCDNB was dissolved in toluene and aminated by the technique mentioned above. In this case, however, the reaction product was insoluble in toluene. Therefore, the reaction mixture was filtered through a fine glass-fritted crucible and the crystals washed with toluene. The residue was then dried under vacuum.

DISCUSSION

INFRARED SPECTRA

Fig. 1 shows the IR spectra of TCTNB, TCDNB, T₄CDNB, and TATB. These materials represent the product (TATB), its precursor (TCTNB), and the two major impurities in the TCTNB. Also shown are the IR spectra of the triaminodinitrochlorobenzene (Species 5) and the triaminodinitrobenzene (Species 6) which were synthesized by the techniques described. These spectra clearly show the successful amination of the TCTNB and the T₄CDNB. Further, spectrum 1e shows the loss of the chloride from the TCDNB ring.

TOTAL CHLORIDE CONTENT

The synthesized products were analyzed for chloride content in order to further verify the identity of the synthesized species. Table I shows the results of these analyses.

(1) W. T. Quinlin, Z. L. Estes, V. H. Evans, and C. L. Schaffer, "TATB Synthesis," MHSMP-75-5H (October-December 1974).

MELTING POINT DETERMINATION

Melting points were determined for the five species of interest and values compared with those reported in the literature (Table II).

THIN-LAYER CHROMATOGRAPHY

The sample was spotted on a Silica-G-Zn plate and eluted with (a) 1,2-dichloroethane and (b) a 1-9 acetone/petroleum ether mixture. Fig. 2 shows the chromatograms obtained. As can be seen, only one spot is obtained in each case, indicating purity of preparation. Also, the position of the spots is consistent with the chromatograms of triamino-dinitrobenzene and triaminodinitrochlorobenzene as determined by Yasuda(2).

CONCLUSION

The two major impurities in TATB—1,3,5-triamino, 2,4-dinitrobenzene, and 1,3,5-triamino,2,4-dinitro,6-chlorobenzene—have been successfully synthesized and identified by IR spectroscopy and thin-layer chromatography. These materials are of sufficient purity for use as analytical standards in the TATB assay.

ACKNOWLEDGEMENT

The authors wish to thank G. E. McGaugh for performing the synthesis.

(2) Yasuda, S. K., "Identification of 1,3,5-Triamino-2,4,6-Trinitrobenzene Impurities by Two Dimensional Thin-Layer Chromatography," *J. Chromatog* 71, 481-86 (1970).

Table I. Total Chlorine Content of TATB Impurity

<u>Sample</u>	<u>Total Cl (%)</u>	
	<u>Theoretical</u>	<u>Measured</u>
Triaminodinitrochlorobenzene	14.32	14.64
Triaminodinitrobenzene	0.00	0.27

Table II. Melting Point Determination

<u>Sample</u>	<u>Melting Point (C)</u>	
	<u>Literature</u>	<u>Found</u>
TCTNB	187	187.4 - 188.9
TCDNB	129.5	131.0 - 131.8
T ₄ CDNB	162	161.5 - 162.9
Triaminodinitrobenzene	321*	MP > 300.5
Triaminodinitrochlorobenzene	315* (Max)	MP > 300.5

**Decomposes*

Fig. 1