Full Paper

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201300090

Testing of DNT and TNT by the Mini-Autoclave Method

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Abstract: Autoclave methods are commonly used when pressure progress under thermal stress is of interest. One of them is the mini-autoclave method by Kühner AG. To test the robustness of the equipment under powerful exposure, two known high energetic materials, DNT and TNT, were investigated. The sample mass was increased stepwise in the range from 0.25 g to 1.0 g. For one test (1 g TNT), gas burners instead of the usually employed 2-zone heating block, were used to intensify the test conditions. Results showed the expected slower pressure generation of DNT in comparison to TNT. The mechanical robustness of the apparatus could be approved in all runs. Pressure data were used to calculate the energy release of decomposition. The values were in good agreement with the heat of decomposition, estimated by DSC.

Keywords: Autoclave · DNT · TNT · Decomposition · Energy

1 Introduction

The mini-autoclave, developed by Kühner AG [1], is commonly used for the Mini Closed Pressure Vessel Test (MCPVT) to estimate condensed phase explosive properties of organic compounds [2, 3]. MCPVT could be used as a screening test for new products, which are considered to have explosive properties. Depending on the result of the screening test, it can be decided, whether further classification procedure for explosives, according to transport regulations, has to be followed or not. A round robin test in 2007 showed the capability of the method [4].

Additionally, the autoclave can be employed for self-reactive substances and organic peroxides to assess the behaviour of these substance groups under defined confinement [5]. The working group "Energetic and Oxidising Substances" (EOS) of IGUS (International Group of Experts on the Explosion Risks of Unstable Substances) discussed over several years the possible implementation of the MCPVT in test series E of the UN Recommendations on the Transport of Dangerous Goods [6]. In test series E potential self-reactive substances of division 4.1 and organic peroxides of division 5.2 are tested for transport classification by determination of the effect of heating under defined confinement. At the experts meeting in 2010 these efforts were temporarily abandoned because too few results were available to establish a classification procedure.

Nevertheless, the MCPVT is still a useful tool for fast screening. Only a small sample amount, as minimum 0.2 g to 2 g maximum, is necessary. In comparison to methods of thermal analyses, e.g. Differential Scanning Calorimetry (DSC), where samples in mg-scale are used, in the MCPVT higher samples' amounts are more representative.

Since the tested substances are potentially highly energetic the autoclave is thickly walled and equipped with a bursting disc to allow pressure release before demolition. Anyhow it is questionable, if the autoclave could be destroyed under extreme conditions. During lifetime of the autoclave at BAM, a wide variety of chemical substances and mixtures have been tested to estimate its decomposition characteristics. At worst the glassy sample holder and the glassy cover of the temperature sensor holder fragmented into powder. Several times capsule detonators were tested (in these cases no glassy parts were used), whereby the temperature sensor holder was deformed once only.

In this paper two substances, a Dinitrotoluene (DNT) isomers mixture and Trinitrotoluene (TNT), with known explosive properties, were studied. Organic substances with nitro-groups are generally known for their hazardous potential, namely high decomposition energy and velocity of decomposition (up to a detonation). Therefore both chemicals were applied to check the mechanical robustness of the test equipment.

Furthermore, the energy content was assessed from the observed maximum pressure. The results were compared with the values of heat of explosion and heat of decomposition, known from literature and from our own measurements.

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2 Experimental Section

2.1 Material

DNT consisted of a mixture of isomers with 96% by weight (analysed at BAM). TNT had military quality with a solidification point higher than 80.2 °C (flakes, bulk density 0.81 g cm^{-3}).

Both samples were characterized at BAM by melting point, extrapolated onset temperature and heat of decomposition with DSC (heating rate 5 K min^{-1}). The results of the analyses and characteristic data from the literature are given in Table 1.

Thermia Shell B oil, a highly refined mineral oil, was used as reference material for the mini-autoclave run. It is thermally stable between room temperature and 400 °C.

2.2 Apparatus

The MCPVT equipment consists of a set of three autoclaves at maximum. Two are used for samples recording temperature and pressure. The third autoclave is filled with a thermal stable reference substance, in our case Thermia Shell B. All three autoclaves are positioned in an aluminium block. This block and a ceramic heater above it act as heating zones which form the oven. The autoclaves can be heated with a defined heating rate or in isoperobolic mode [1].

The sample is enclosed in the autoclave and thermally stressed to evaluate the thermal stability under enclosure. The maximum pressure (p_{max}), the pressure release per time unit (dp/dt), the temperature range of decomposition and the assessment of gas generation are of interest.

The individual autoclave has an internal volume of 6 mL. To avoid interactions between the sample and the stainless steel autoclave, glassy sample holders are used. Sample mass can vary from 0.2 g to 2 g. Typically, 1 g is used.

The temperature sensor is located in a stainless steel bracket. To prevent contact with the tested sample, it is covered with glass. The pressure sensor is connected to the lid of the autoclave with a 1/16" capillary tube, which was filled with Thermia Shell B for better pressure propagation. For the tests a 40 MPa piezo-resistive pressure transducer from Keller AG was applied.

Temperature and pressure data were collected with 1 Hz in general. In contrast to the original assembly, pressure recording was upgraded. Parallel to the 1 Hz recording, equipment was established to adjust data with a frequency up to 10 kHz.

In using the oven, tests were performed with sample masses of 0.25 g, 0.5 g, 0.75 g of DNT and TNT, respectively. A heating rate of 2.4 K min^{-1} was set. TNT with a sample mass of 1 g sample was tested with a different heating device due to a possible deformation or bursting of the autoclave during the run and possible damage to the oven. For this specific run, one autoclave was heated with three gas burners similar to the Koenen test, Test series E, test E.1 [6]. The test arrangement is shown in Figure 1. One burner was installed below the autoclave. The two other burners were arranged on opposite sides of the autoclave. The autoclave was suspended between two rods and clamped at the lid. The heating rate for the run with 1 g TNT was determined with Thermia Shell B in a reference test in advance.

It was about 150 K min^{-1} in a temperature range between 80 °C and 250 °C. The autoclave was equipped with

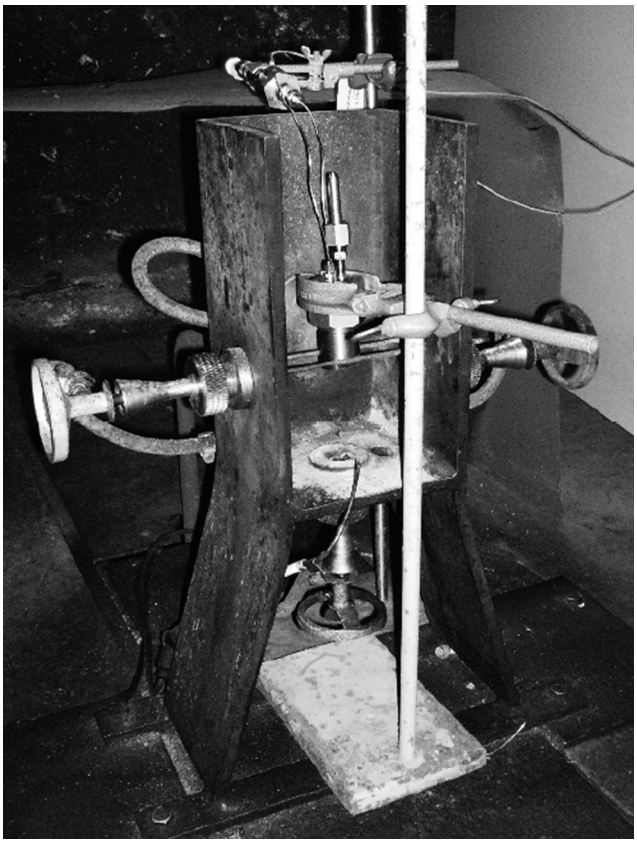

Figure 1. Assembly for measuring 1 g TNT.

Table 1. Characteristic data for DNT and TNT.

Material	DNT mixture	TNT
CAS number	2,4-isomer: 121-14-2 2,6-isomer: 606-20-2	118-96-7
Molecular weight [g mol^{-1}]	182.14	227.1
Oxygen balance [%]	−114	−74
Melting point [°C]	38 (BAM)	81 (BAM)
T_{onset} extrapolated [°C]	306 (BAM)	301 (BAM)
Heat of decomposition [kJ kg^{-1}]	3900 (BAM)	4690 (BAM)
Decomposition temperature [°C]	360 [7]	300 [7]
Volume of detonation gases [dm^3 kg^{-1}]	807 [7]	825 [7]
Lead block test [cm^3 10 g^{-1}]	240 [7]	300 [7]
Velocity of detonation [m s^{-1}]	3750 at 1.0 g cm^{-3} [8, 9]	6900 at 1.6 g cm^{-3} [7]

a bursting disc with an opening pressure of 36 MPa at 20 °C. The run was carried out in a bunker. Simultaneous ignition of burners was started from outside the bunker. A window allowed visual observation.

3 Results and Discussion

In the following temperature and pressure progression during the runs and the calculated energy release are shown.

Figure 2 and Figure 3 display the temperature progression (ΔT) for DNT and TNT runs, respectively (sample masses 0.25 g, 0.5 g, 0.75 g). The difference between the temperature of the sample and the temperature of the reference sample (Thermia Shell B oil) is plotted as ΔT in dependency on the temperature of the reference oil. As expected, the use of larger samples resulted in higher increase of temperature during decomposition. This was observed also for sample masses of 0.75 g DNT and 0.5 g TNT, even though the bursting disc ruptured. The increase in temperature for 0.75 g TNT, where the bursting disc ruptured too, was rather low. This phenomenon is attributed to a very fast pressure release and a synchronous release of heat.

Temperature and pressure progression (1 Hz recording) in dependency of time for the 1 g sample of TNT is given in Figure 4. Because of the high energy input by the burners and the resulting higher heating rate compared to the normal heating procedure, it took only 200 seconds until the bursting disc ruptured. For parts of a second a flash was observed. Decomposition products of TNT, i.e. carbon-containing products and carbon [10], which where emitted when the bursting disc ruptured and the content of autoclave was spread finely, combusted. The autoclave itself was not damaged. After cooling down and opening of the autoclave no demolition of the glass parts was found. The

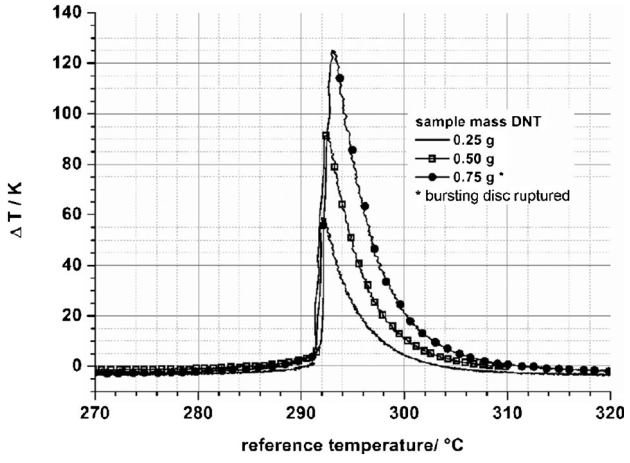

Figure 2. Temperature progression during DNT runs with different sample masses, heating rate 2.4 K min^{-1}.

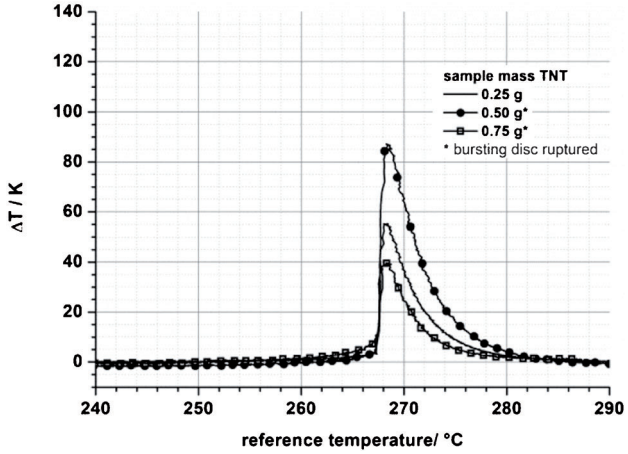

Figure 3. Temperature progression during TNT runs with different sample masses, heating rate 2.4 K min^{-1}.

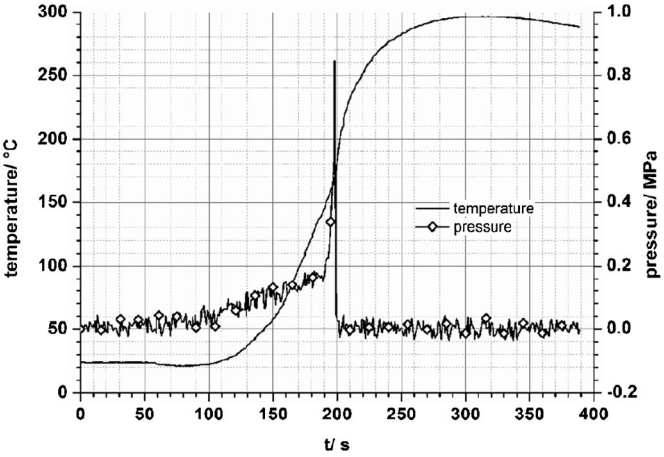

Figure 4. Temperature and pressure progression during run of 1 g TNT and a heating rate about 150 K min^{-1}.

temperature junction was not deformed. All inner parts were covered with a black semi-gloss coating. Such kind of coating was observed in all runs with TNT.

Figure 5 and Figure 6 present the pressure progression for all tests with DNT and TNT, recorded with high frequency (10 kHz). Pressure recording above 40 MPa was not possible due to limitation of the sensor's measuring range. Therefore, curves cannot be shown above this value. This is the case in the tests with 0.75 g DNT and 0.5 g, 0.75 g and 1 g TNT, respectively. In all these cases the bursting disc ruptured. The pressure sensor remained intact, recording the pressure course when the pressure decreased below 40 MPa again. The diagrams show the expected slower decomposition of DNT compared to TNT. The values are given in Table 2.

To compare the pressure progression for DNT and TNT the same time scale was set in the corresponding Figure 5 and Figure 6. Therefore, the pressure curves of 0.75 g and 1.00 g in Figure 6 cannot be discriminated graphically, even

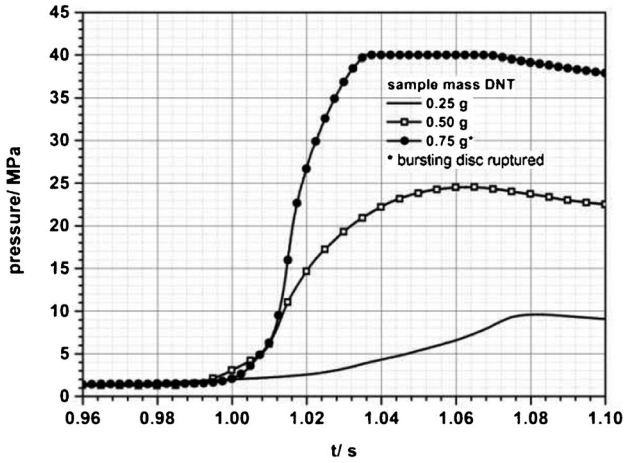

Figure 5. Pressure progression during DNT runs with different sample masses, heating rate 2.4 K min^{-1}.

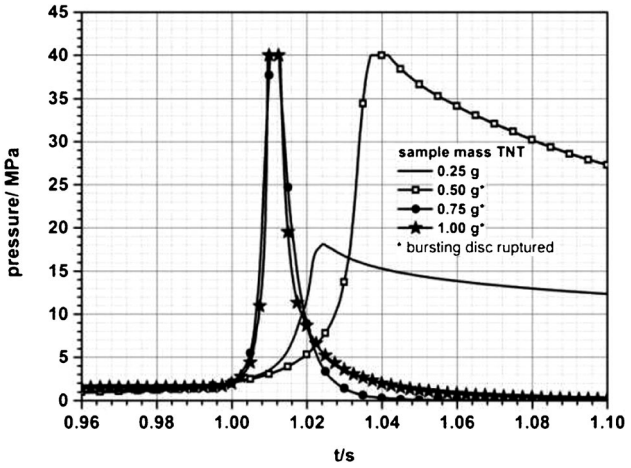

Figure 6. Pressure progression during TNT runs with different sample masses, heating rate 2.4 K min^{-1}, except 1 g (heating rate about 150 K min^{-1}).

Table 2. Maximum rate of pressure rise and maximum pressure for DNT runs with different sample masses, heating rate 2.4 K min^{-1}.

DNT sample mass [g]	T_{onset} extrapolated [°C]	$(dp/dt)_{max}$ [MPa s^{-1}]	p_{max} [MPa]
0.25	288	185	9.5
0.50	288	1330	24.5
0.75	288	2250	45.0 assessed

though the heating rates differed extremely. The values of $(dp/dt)_{max}$ for the two runs, given in Table 2, clearly show the faster pressure progression in the run with higher sample mass and heating rate.

For the runs with a heating rate of 2.4 K min^{-1}, in which the bursting disc ruptured, maximum pressure could not be recorded because of the limited measuring range of the pressure transducer. The values in Table 2 and Table 3, which are denoted as *assessed*, were deduced from the decreasing slope of the corresponding pressure curve.

Table 3. Maximum rate of pressure rise and maximum pressure for TNT runs with different sample masses, heating rate 2.4 K min^{-1}, except 1 g TNT (heating rate about 150 K min^{-1}).

TNT sample mass [g]	T_{onset} extrapolated [°C]	$(dp/dt)_{max}$ [MPa s^{-1}]	p_{max} [MPa]
0.25	267	4200	18
0.50	268	6050	42 assessed
0.75	267	≈9500	50 assessed
1.00	–	≈45000	–

According to the proposed analysis of MCPVT results by Whitmore [4], both DNT (assuming that 1 g would produce an even higher $(dp/dt)_{max}$ than 0.75 g) and TNT match the explosive rank A, as expected.

Comparison of the extrapolated onset temperatures, estimated with the MCPVT, with the corresponding DSC values shows that the MCPVT values are more conservative than the ones from DSC.

Based on the MCPVT runs and the measured pressure courses, the released energy amount E was calculated following Equation (1) [11].

$$E = \frac{pV}{0.1388} \ [J] \qquad (1)$$

V corresponds to the inner free volume of the autoclave in m^3 ($V = 6 \times 10^{-6}$ m^3), p is the maximum pressure in Pa. Energy was calculated for 0.25 g, 0.50 g and 0.75 g of DNT and TNT, respectively. The energy values, shown in Table 4, are correlated to the individual sample mass.

For DNT the calculated energy lies in the range between 1600 kJ kg^{-1} and 2600 kJ kg^{-1}. For TNT the energy covers a range between 2800 kJ kg^{-1} and 3600 kJ kg^{-1}. A depend-

Table 4. Energy values for DNT mixture and TNT.

	DNT mixture	TNT
Energy content [kJ kg^{-1}]	1642	3112
calculated after Ref. [11]	2118	3631
	2594	2882
Heat of combustion [kJ kg^{-1}]	18683 (BAM)	14778 (BAM)
	2,4-isomer: 19 518 [14]	15 015 [14]
	2,6-isomer: 19551 [14]	
Heat of explosion [kJ kg^{-1}]	2703 (BAM)	2817 (BAM)
	2,4-isomer: 3192 [7]	4564 [7]
	2,6-isomer: 3325 [7]	
Heat of decomposition [kJ kg^{-1}]	3900 (BAM)	4690 (BAM)
Gurney energy [kJ kg^{-1}][1]	–	2240 [15]

ency on the sample mass could be supposed for DNT, while this is not observed for TNT. This latter fact could be put down to the inaccurately assessed maximum pressure values.

For a comparison with other energy types, the heat of combustion, according to DIN 51900 part 3 [12], was determined at BAM and is given with additional literature values in Table 4. For both substances the determined values are in good agreement with the literature.

Furthermore, the heat of explosion was estimated with an adiabatic calorimeter, based on TL 1376-0600 [13]. Literature values for the heat of explosion are higher than the measured ones. As it can be seen, the measured value of heat of explosion for DNT and in particular for TNT, are lower than the calculated values given in the literature [7]. It is assumed that the reaction is not completed during the test run in the calorimetric bomb, since the used sample mass is quite low and the measurements are carried out without confinement. The problem of getting low values of heat of explosion, when using this method is already known in literature [16].

In addition to the above mentioned energy types, the Gurney energy of TNT was taken from literature. The Gurney energy reflects the impulse of a detonation. All these data are listed in Table 4.

The heat of combustion is remarkable higher than the calculated energy content. Due to the different ratio of sample mass to volume in the mini-autoclave and, on the other side, the apparatus for estimating the heat of combustion, the oxygen content in the devices is different. The available oxygen content, related to the sample mass, in the mini-autoclave is considerably lower. It can be assumed that combustion in the mini-autoclave does not play a significant role. The low energy values, calculated from the MCPVT runs, indicate a reaction without oxygen and/or an incomplete reaction. Edge effects also occur and affect the result.

The calculated energy content, deduced from MCPVT measurements should be comparable to the heat of explosion and the heat of decomposition. The MCPVT results are partly higher than the estimated values with the calorimetric bomb. However, they are not as high as the calculated heat of explosion values and the measured DSC results. With higher sample mass and therefore higher maximum pressure, the MCPVT results are more similar to the calculated values of heat of explosion and measured heat of decomposition. As mentioned above, small sample mass and edge effects influence the result.

The Gurney energy as a measure of the impulse of detonation is, as expected, smaller than the heat of explosion and the heat of decomposition.

4 Conclusion

Measurements with the MCPVT allow the estimation of critical temperatures and pressures for energetic materials. Temperature and pressure progression give valuable information about energy and gas release under defined confinement. The heating rate strongly affects the reaction velocity. This is reflected by the measured temperature rate (dT/dt) and pressure rate (dp/dt). However, it is possible to assess the reaction velocity in a relative manner to already known reactions or decompositions.

DNT and even more TNT, as highly energetic substances, showed the expected fast decomposition during heating under defined confinement.

Despite of the used heating rate (150 $K\,min^{-1}$) for 1 g TNT, which was up to 60 times higher than for the normal test procedure (2.4 $K\,min^{-1}$), the mini-autoclave was neither destroyed nor were parts of the lid damaged.

When a common sample mass for the MCPVT is used, namely up to 1 g, the energy content of the sample is small, even for detonable explosives and at insufficient venting. Strong damage of the autoclave and formation of fragments could be excluded. The stressing of sample containers' walls is in the border range of elastic and plastic deformation.

Nevertheless, the possibility of bursting disc rupture, pressure release, ignition of released vapour or gas and possibility of flammability requires the MCPVT to be carried out in such a way that no hazard to individuals can occur.

An approximation of the energy content based on assessed maximum pressure seems to be difficult at least for the tested examples of DNT and TNT. Compared to the literature and theoretical values, the approximated energy content by MCPVT is obviously lower. This could be explained by edge effects and incomplete conversion. For the TNT sample, the energy content, deduced from MCPVT runs, is in agreement with the measured heat of explosion.

Acknowledgments

The authors would like to take the opportunity to express their gratitude to the late Thomas Bischof, who carried out the majority of the mini-autoclave tests over the last years. We thank Mrs. K. Wegener and Mr. D. Weinert for estimation of heat of combustion and of explosion, Dr. A. Berger and Mrs. B. Fourier for the DSC measurements. Furthermore thanks to Dr. Pfeifer for NMR spectroscopic measurements.

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Received: July 24, 2013
Revised: November 27, 2013
Published online: January 22, 2014

