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THE EXPLOSIVE PROPERTIES OF THE
AMINO-SUBSTITUTED, SYMMETRICAL
TRINITROBENZENES (U)

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THE EXPLOSIVE PROPERTIES OF THE AMINO-SUBSTITUTED,
SYMMETRICAL TRINITROBENZENES (U)

By N. L. Coleburn, E. E. Drimmer

ABSTRACT: The shock sensitivity and failure diameters of four explosive compounds of the trinitrobenzene series: 1, 3, 5-trinitrobenzene (TNB), 1-amino 2,4,6-trinitrobenzene (TNA), 1,3-diamino 2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino 2,4,6-trinitrobenzene (TATB) are functions of the number of amino groups, heats of formation and oxygen balance. The most sensitive, TNB, has the lowest heat of formation and oxygen balance. Detonation failure occurs at diameters of ≤ 0.3 cm TNB, 0.3 cm TNA, 0.53 cm DATB and 1.3 cm TATB. The detonation velocity-charge density relation, $D(\text{m/sec}) = 2480 + 2852 \rho(\text{g/cm}^3)$, and the measured detonation energies of 815 ± 15 cal/g are the same for each series member. The measured detonation pressures are 259.4 kb and 174.6 kb for TATB at densities of 1.60 g/cm³ and 1.50 g/cm³, 251.0 kb for DATB at 1.80 g/cm³, and 219.2 kb for TNB at 1.64 g/cm³. Rapidly applied shocks, with peak pressures as high as 100 kilobars in the NOL wedge test, fail to detonate 12.7 mm thick TATB samples. On the other hand, under such shock conditions, the other three compounds are at least as sensitive as Composition B. Each, however, is less sensitive than pressed TNT to slowly applied pressure pulses such as might develop in an impact accident.

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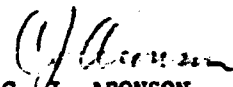
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May 1963

THE EXPLOSIVE PROPERTIES OF THE AMINO-SUBSTITUTED, SYMMETRICAL
TRINITROBENZENES (U)

The purpose of this work was to study the effect of systematic changes in molecular structure on the shock sensitivity and detonation properties of a chemically-related series of explosives. The results of this approach should be of value to the synthetic organic chemist and the research worker concerned with sensitivity of explosives and propellants. The work was done under WepTask No. RUME 4E 000/212-1/F008-10-004, Study of Explosive Properties.

R. E. ODENING
Captain, USN
Commander


C. J. ARONSON
By direction

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1. INTRODUCTION

1.1 Previous Studies. Several studies have been reported correlating the chemical structures of explosive organic compounds with their thermal stabilities (1,2)*, impact sensitivities (3,4,5), and other explosive properties. Perhaps most pertinent to the results reported in the present paper is Robertson's work (2) in 1921, wherein thermal stability, detonability, and shock sensitivity were related to the heats of formation of several organic explosive compounds whose compositions were varied by substitution of various alkyl groups. Forty years later Blinov (5) reported the sensitivity of various dinitro-compounds of benzene to impact, friction, heat, and flame. In each of these studies, the duration of the explosion initiating stimulus was generally of the order of milliseconds. Under such long duration stimuli, many workers (e.g. 6,7,8) consider the explosive response (such as a "go" in the impact hammer machine) a phenomenon intermediate between a thermal decomposition and a detonation. On the other hand, initiation to detonation may occur in times of the order of a microsecond or less, when the stimulus is applied by means of a shock wave transmitted through air (9), water (10,11), or solids (12,13,14). Comparison of the response of members of a chemically related series of compounds to such more rapidly applied stimuli had not yet been made. This paper will discuss such a set of data.

1.2 The Amino-Substituted Trinitrobenzenes. A group of four chemically related explosive compounds can be considered to have been formed by the substitution, one at a time, of an amino (NH_2) group for a hydrogen, in symmetrical trinitrobenzene.

1,3,5-trinitrobenzene -----	TMB
1-amino-2,4,6-trinitrobenzene -----	TMA**
1,3-diamino-2,4,6-trinitrobenzene -----	DATB
1,3,5-triamino-2,4,6-trinitrobenzene -----	TATB

(The initials on the right are those commonly used to identify the particular compounds.) These compounds are well known from the chemical literature (15, 16, 17). For ready reference, their various physical, chemical and explosive properties have been assembled and tabulated in Table 1 (together with the

* References will be found on page 23.

**Another name for this compound is "2,4,6-trinitroaniline," from which "TMA" is derived. Even more commonly, this compound is known as picramide.

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TABLE 1
Physical, Chemical, and Explosive Properties

Property	TNB	TAA	DATB	TATB	TNT
Structural Formula					
Molecular Weight	213	228	243	258	227
Crystal Density (g/cm ³)	1.668	1.762	1.837	1.938	1.651
Melting Point (°C)	121	188	286	450d	81
Heat of Formation (kcal/mole)	-11.40 (18)	-20.07 (19)	-29.23 (20)	-36.85 (20)	-17.81
Activation Energy (kcal/mole)	--	--	65.8 (21)	--	37.0 (21)
Specific Heat (cal/g/°C)	--	--	0.261 (21)	--	0.264 (21)
Thermal Conductivity (10 ⁻⁴ cal/sec/cm-°C)	--	--	6.19 (21)	--	4.61 (21)
Vacuum Stability	0.0	0.0	0.1	0.1	<0.1
100°C (cm ³ /g/48 hr)	<0.10	--	5.4	0.8	--
260°C (cm ³ /g/hr); 2 hr exposure	--	--	52.5 (22)	4.5 (22)	--
280°C (cm ³ /g/hr); 2 hr exposure	--	1.74	1.800	1.802	1.619
Experimental Density (g/cm ³)	1.64	7440	7600	7658	6700
Detonation Velocity (m/sec)	7269	2852	2852	2852	3225 (23)
(at expt. density)	2852	0.3	0.53	1.3	187
40/dp (m/sec)/(g/cm ³)	<0.3	241*	251	259	692
Failure Diameter (cm)	219.2	627	800	829	200
Detonation Pressure (kb)	811	177	>320	>320	200
Detonation Energy (cal/g)	100	2347**	3028	3124	2830
50% Impact-Sensit Height (cm)	2946	--	3130	3229	2930
Plate Push Value (ft/sec)	--	--	--	--	--
At 95% crystal density	--	--	--	--	--
At 98% crystal density	--	--	--	--	--

d - decomposes

* Calculated from $P = \rho^2/4$

** TAA/tytel 95/5 (Plastic-bonded explosive)

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properties of TNT for comparison), and therefore only a brief description of each is given here.

Trinitrobenzene is a yellow solid of crystal density, 1.688 g/cm^3 . Perhaps because of its resonating molecular structure, which permits intramolecular bonding, TNB is one of the most heat stable explosives known. When heated, TNB gives off only a trace of gas at 180°C , nearly 60°C above its melting point, evolves less than $0.1 \text{ cm}^3/\text{g/hr}$ at 260°C (2) and does not explode until 520°C (1). TNB can be made from trinitrotoluene (TNT) by oxidation and decarboxylation of the resulting trinitrobenzoic acid. Kast (24) measured the detonation velocity as a function of charge density for trinitrobenzene using the Dautriche method. Koehler and Desvergues (25) also used this method to measure a velocity of 7441 m/sec for cast TNB, some 2 percent above our value (below).

TNA, picramide, is a yellow, needle-like solid melting at 188°C . Its crystal density is 1.762 g/cm^3 . It can be prepared by nitrating aniline in glacial acetic acid. Brisance (3) is the only explosive property reported to date for picramide.

The NOL synthesis (26) and related studies (27, 28) of DATB and TATB have renewed interest in these heat resistant explosives. DATB has a crystal density of 1.837 g/cm^3 (23°C), melts at 286°C , and although less stable than TNB, decomposes at a negligible rate at 204°C (24). TATB, the most dense member of the series (crystal density, 1.938 g/cm^3), has the highest melting point, 450°C , and is the least sensitive to mechanical shocks.

2. DETONATION VELOCITY MEASUREMENTS

2.1 Charge Preparation. For charges with densities from 1.6 to 1.9 g/cm^3 , 5.0-cm diameter pellets were obtained by standard pressing techniques and then machined to smaller diameters as necessary for the specific individual tests. Charges with densities from 1.2 to 1.5 g/cm^3 were obtained by press loading (at pressures up to $8,000$ - $10,000 \text{ psi}$) 15-gram increments of the compound into 4.4 to 5.4-cm internal diameter, 0.15-cm thick, copper or aluminum tubes*. Charges with densities below 1.2 g/cm^3 were prepared by hand-packing the material into pyrex glass tubing. The detonation wave from charges confined in the metal tubes was observed through a series of small, evenly spaced holes drilled through the metal casing. The initiating explosive train consisted of a U.S. Engineer's Special Electric Detonator, a 5.1-cm diameter plane-wave generator (Baratol-Composition B), and a 5.1-cm diameter, 5.1-cm long tetryl pellet.

* With the exception of 2 shots confined in Lucite (Table 4, nos. 3 and 4) in which the explosive was pelleted and slipped into the confining Lucite tube.

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2.2 Detonation Velocity-Charge Density Relationship. The measured detonation velocities of each series member are listed in Tables 2 to 5, and are plotted in Figure 1. The line drawn through the data represents the measurements previously reported (28) for DATB whose detonation velocity varies linearly with charge density according to

$$D = 2480 + 2852 \rho \quad (\pm 25 \text{ m/sec}) \quad (1)$$

Velocities of the other series members have an average deviation of 50 m/sec from this line. The agreement indicates the detonation velocity-charge density relationship is the same for all members of the series: detonation velocity is very insensitive to the number of amine groups.

2.3 Failure Diameter. The failure diameter was determined by detonating pyramidal charges consisting of three cylindrical pellets, 2.54, 1.22, and 0.64-cm diameter, stacked in order of decreasing diameter. On top of the 0.64-cm diameter pellet was placed a 1.25-cm long, truncated conical section, tapering from 0.64-cm diameter at its base to 0.32-cm at the top. The conical section was not used with trinitrobenzene because of machining difficulties. Detonation of the pyramidal charges of TATB, DATB and TNA gave normal velocities, with detonation failure occurring at charge diameters: 1.3 cm (TATB), 0.53 cm (DATB), and 0.3 cm (TNA). The failure diameter of trinitrobenzene was not ascertained by this method. However detonation propagated without measurable diminution of rate up to the end of 3.8-cm long, 0.6-cm diameter TNB pellets.

3. MEASUREMENTS OF THE CHAPMAN-JOUQUET PRESSURES

3.1 Experimental Method. The Chapman-Jouquet pressures were experimentally determined using the water tank, or aquarium technique (29). For convenience, this method is described briefly: the lower end of a cylindrical charge is immersed to a depth of 6 cm in distilled water. The upper end of the charge, protruding above the surface, is initiated to detonation by a plane-wave generator. As a result, the detonation wave strikes the water at normal incidence, and a shock wave is transmitted into the water. The shadowgraph of the shock wave in the water is recorded by a rotating-mirror smear camera using collimated light from an electrically exploded wire light source. Analysis of the record then yields the velocity of the shock in the water as a function of distance from the bottom of the charge. The velocity (U_{H_2O}) of this shock at the water-charge interface is then obtained by extrapolation. Having U_{H_2O} the equation of state of water (30) is employed to get the particle velocity (u_{H_2O}) and the peak pressure (P_{H_2O}) in the water at the water

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TABLE 2
Detonation Velocity of Trinitrobenzene (TNB)

Charge No.	Diameter (cm)	Length (cm)	Confinement	Density (g/cm ³)	Detonation Velocity (m/sec)
1*	0.64	2.54	None	1.670	7160
	0.64	1.27	"	1.670	7160
	1.27	1.30	"	1.657	7160
	1.27	1.35	"	1.657	7160
	2.54	2.39	"	1.662	7160
	2.54	2.56	"	1.662	7160
	2.54	2.54	"	1.662	7160
	2.54	2.39	"	1.647	7160
2	5.24	15.1	Copper	1.264	6090
3	5.24	15.1	"	1.234	6100
4	5.24	15.1	"	1.265	5905
5	4.62	13.7	Glass	1.644	7269

* Charge 1 was in the form of a pyramid, made of cylinders.

TABLE 3
Detonation Velocity of Picramide (TNA)

Charge No.	Diameter (cm)	Length (cm)	Confinement	Density (g/cm ³)	Detonation Velocity (m/sec)
1*	Conical**	2.34	None	1.726	--
	0.64	1.34	"	1.726	7345
	1.27	1.34	"	1.746	7310
	1.27	2.76	"	1.750	7310
	2.54	2.76	"	1.737	7560
	2.54	2.74	"	1.746	7560
	2.54	2.74	"	1.744	7560
	2.54	2.77	"	1.728	7560
2	4.43	15.24	Copper	1.485	6800

* Charge 1 was in the form of a pyramid, consisting of one conical, and three cylindrical sections.

**Diameter uniformly decreased from 0.63 cm to 0.32 over 2.34-cm length.

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TABLE 4
Detonation Velocity of DATB

Charge No.	Diameter (cm)	Length (cm)	Confinement	Density (g/cm ³)	Detonation Velocity (m/sec)
1*	Conical**	1.250	None	1.816	***
	0.64	2.540	"	1.816	7620
	1.27	2.644	"	1.815	7620
	2.54	7.861	"	1.809	7620
2	5.47	13.40	Glass	0.901	5050
3	5.47	15.31	Lucite****	1.427	6600
4	4.48	15.53	"	1.375	6470
5	4.44	15.26	Aluminum	1.381	6470
6	4.44	15.27	"	1.285	6130
7	4.44	15.27	"	1.205	5880
8	5.08	15.80	None	1.788	7570
9	5.08	20.47	"	1.793	7580

* Charge 1 was in the form of pyramid, made of cylinders, plus a conical apex.

** Diameter uniformly decreased from 0.64 to 0.32 cm over 1.25 cm length.

*** Failure diameter = 0.53 cm.

**** Wall thickness - 0.20 cm.

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TABLE 5
Detonation Velocity of TATB

Charge No.	Diameter (cm)	Length (cm)	Confinement	Density (g/cm ³)	Detonation Velocity (m/sec)
1*	Conical	0.64	None	1.880	--
	0.64	1.27	"	1.881	--
(Boostered	1.27	1.32	"	1.874	7610
by 75/25	1.27	1.35	"	1.879	7610
Cyclotol)	1.27	1.35	"	1.880	7610
	1.27	1.32	"	1.878	7614
	2.54	2.57	"	1.882	7772
	2.54	2.57	"	1.875	7772
2**	Conical		None	1.864	7650
	1.27	2.54	"	1.863	7650
(Boostered	2.54	2.54	"	1.860	7745
by Tetryl)	2.54	2.54	"	1.864	7745
	5.08	5.08	"	1.862	7745
	5.08	5.08	"	1.864	7745
3	5.08	5.08	Glass	1.802	7658
4	4.45	15.24	Glass	1.508	6555

- * Tapered to 0.31 cm from 0.64 cm over 0.64 cm length.
Detonation did not propagate into 0.64-cm diameter section.
- ** Tapered to 0.64-cm diameter from 1.27-cm diameter over
1.9-cm length.

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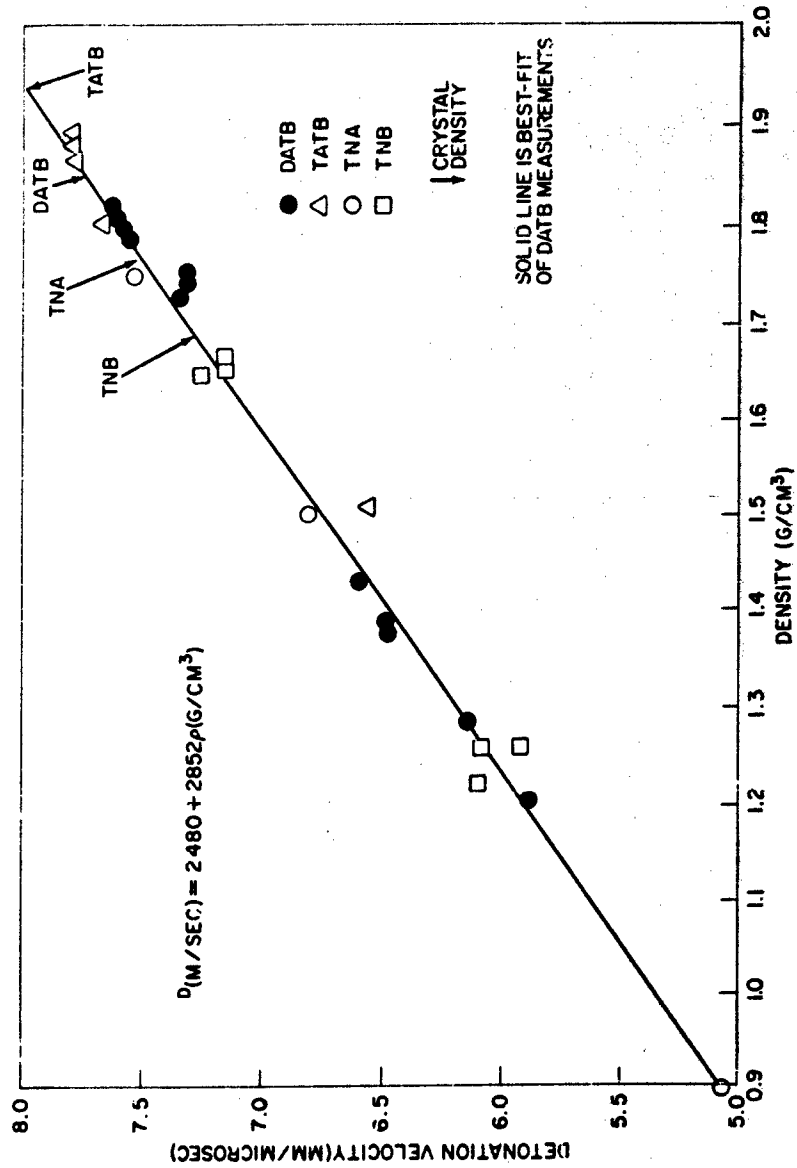


FIG. 1 DETONATION VELOCITY AS A FUNCTION OF CHARGE DENSITY.

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explosive interface. The Chapman-Jouguet pressure for the explosive is then obtained by iterating values of "k" (the isentropic exponent of the product gas expansion) between two relations that are derivable (29) from the Riemann postulate as applied to an isentropic expansion of the product gases until the same P_{CJ} is obtained from both equations:

$$P_{CJ} = \frac{\rho_0 D^2}{k+1} \quad (2)$$

and

$$P_{CJ} = P_{H_2O} \left[1 - \frac{(k^2-1) U_{H_2O} - (k-1) D}{2kD} \right]^{-\frac{2k}{k-1}} \quad (3)$$

Here, as usual, D represents the detonation velocity of the explosive, and ρ_0 is its density before detonation.

Using an equation derived by Jacobs (31) and Price (32) the experimentally determined values of D and k permit a calculation of the energy of detonation, Q.

$$Q = D^2/2 (k^2-1) \quad (4)$$

3.2 Results. Values of the detonation parameters obtained by this water shock method for (normal charge densities) DATB, TATB, and one plastic-bonded composition of DATB, are listed in Table 6 where they are compared with those of TNT. These measurements are considered to be correct to within 1% in shock velocity, leading to relative errors of approximately 3 percent in the Chapman-Jouguet pressure, 3 percent in k, and 6 percent in detonation energy.

4. DETONATION CALCULATIONS

4.1 Heats of Reaction. The heat of reaction, Q, can be estimated if one assumes that on detonation, the order of forming the product gases is $H_2O(g)$, $CO(g)$, $CO_2(g)$

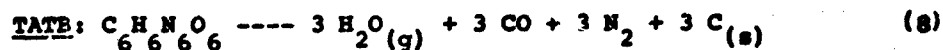
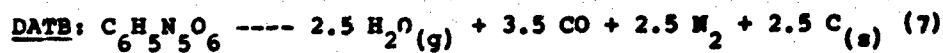
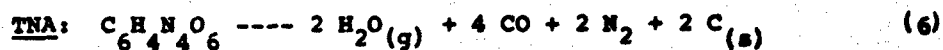
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TABLE 6
Chapman-Jouguet Pressure, Energy, and Isentropic Exponent
From Water-Shock Measurements

Explosive	ρ (g/cm ³)	D (m/sec)	U_{H_2O} (m/sec)	u_{H_2O} (m/sec)	P_{H_2O} (at HE-H ₂ O interface) (kb)	P_{CJ} (kb)	k	Q (cal/g)
TNB	1.64	7269	5835	2522	147.0	219.2	2.96	811
DATB	1.79	7585	5980	2624	156.9	251.0	3.10	800
DATB/Zytel (95/5)	1.71	7200	5839	2524	147.4	224.0	2.97	792
TATB	1.80	7658	6071	2685	163.0	259.4	3.07	829
TATB	1.50	6555	5519	2303	126.9	174.6	2.71	808
TMT	1.62	6790	5532	2312	127.6	187.2	2.99	692

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C(s) (if there is insufficient oxygen to form CO₂) (33, 34, 35, 36). With this assumption, the reactions would be



The measured heats of formation (18, 19, 20) are

$$\Delta H_{(\text{TNB})} = -11.40 \text{ k cal/mole.}$$

$$\Delta H_{(\text{TNA})} = -20.07 \text{ k cal/mole.}$$

$$\Delta H_{(\text{DATB})} = -29.23 \text{ k cal/mole.}$$

$$\Delta H_{(\text{TATB})} = -36.85 \text{ k cal/mole.}$$

Using the heat-of-formation data (37) of the decomposition products, the heats of reaction are calculated to be as follows, with the detonation energy from the aquarium measurements (Table 6) shown in parenthesis:

$$Q_{(\text{TNB})} = 937 \text{ cal/g (811).}$$

$$Q_{(\text{TNA})} = 903 \text{ cal/g.}$$

$$Q_{(\text{DATB})} = 875 \text{ cal/g (800).}$$

$$Q_{(\text{TATB})} = 857 \text{ cal/g (82%).}$$

The calculated Q values over estimate the experimental detonation energies by 3 percent for TATB, 9 percent for DATB and 13 percent for TNB. The calculated values decrease as the molecular weight of the species increases but the trend in the

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experimental values indicates the detonation energy is approximately the same for each series member.

4.2 Halford-Kistiakowsky-Wilson Equation of State. By following the calculation scheme outlined in Appendix A, the Halford-Kistiakowsky-Wilson (HKW) equation of state (33) was used to obtain theoretical values of the detonation parameters for these compounds, Table 7.

TABLE 7

Calculated Detonation Parameters

Compound	ρ_0 (g/cm ³)	D (m/sec)	P (kb)	V (cm ³ /g)	T (°K)	Q (cal/g)
TNB	1.6	7082	181.4	.4837	2950	937
TNA	1.6	7055	179.8	.4839	2839	903
DATB	1.6	7010	170.3	.4865	2638	875
TATB	1.6	7055	171.2	.4906	2574	857

The constant detonation velocity of 7050 (constant to 0.6%) meters per second obtained for the four compounds is in agreement with the experimental data first, in that the velocities for all, at a given initial density, are equal; and second, at the initial density of 1.60 g/cm³ the experimentally observed velocity was 7040 m/sec. This unusually-close agreement between the calculated and observed detonation velocity values testify to the applicability of the HKW equation of state to the detonation reactions of organic explosives of the type discussed in this report.

The calculated detonation pressures appear to be about 15 per cent low, compared to the values experimentally obtained with shocked water as the pressure-measuring device. Further refinement of the data, both theoretical and experimental, will have to be performed before this difference can be reconciled.

The detonation temperatures, ranging from 2574 for TATB to 2950 for TNB, are consistent with the decrease in the detonation energy calculated as the molecular weight of the species increases.

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5. SENSITIVITY TO SLOWLY APPLIED SHOCKS

5.1 Impact Sensitivity and Oxygen Balance. The sensitivity of the explosives in this chemically related series, to relatively slowly applied, low pressure, mechanical shocks (as are developed in the impact hammer test), shows a monotonic decrease, with an increase in the number of amino groups. TNB and picramide have impact sensitivities (50% points) of 103 and 177 cm respectively on the NOL impact hammer machine (38); TATB and DATB do not initiate, even at the maximum height (320 cm) of the NOL machine. This ordering of sensitivity of the compounds is the same as the ordering of their heats of formation: the most sensitive, TNB, has the lowest heat of formation. As demonstrated by Kamlet (4) a correlation exists between impact sensitivity and oxygen balance for structurally related groups of explosives containing C-NO₂ or N-NO₂ bonds. This correlation for TNB, TNA, DATB and TATB² is shown in Table 8 where the oxygen balance (to CO) per 100 grams of the compound (i.e., OB/100) has been computed by the equation,

$$OB/100 = \frac{100 (2n_O - n_H - 2n_C)}{\text{Mole Wt. H.E.}} \quad (9)$$

and the n's represent the number of atoms of the particular element, in one molecule of explosive.

TABLE 8
Correlation of Impact Sensitivity with Oxygen
Balance and Heat of Formation

Compound	Molecular Formula	Mole Wt.	HFE (K cal/mole)	OB 100g	Impact Sensitivity* Height (cm)
TNB	C ₆ H ₃ N ₃ O ₆	213	-11.40	-1.40	103
TNA	C ₆ H ₄ N ₄ O ₆	228	-20.07	-1.75	177
DATB	C ₆ H ₅ N ₅ O ₆	243	-29.23	-2.06	>320
TATB	C ₆ H ₆ N ₆ O ₆	258	-36.85	-2.33	>320

*Reference (38)

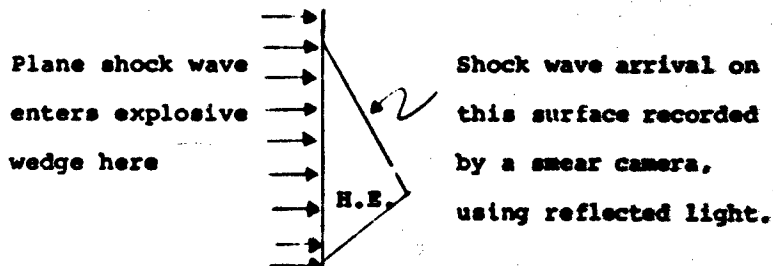
Thus, in Table 8, the (absolute) OB/100 value increases from 1.40 (TNB) to 2.33 (TATB) as the impact hammer values increase from 103 (TNB) to >320 (TATB).

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The impact hammer data shows that all members of this series of compounds are considerably less sensitive to mechanical shocks of this type than Composition B (impact hammer 50 percent point equals 65 ± 5 cm). As will be seen shortly, when the pressure pulse is delivered more rapidly as in the transmission of a shock wave, the sensitivities of several of these compounds are very similar to that of Composition B.

6. SENSITIVITY TO RAPIDLY APPLIED SHOCKS

6.1 Wedge Test Measurements. The initiation of detonation in solid explosives by shock waves transmitted through air, water, or solids, generally occurs within a few microseconds. The NOL wedge test (12, 28) is designed to study within such short times, the details of the build-up-to-detonation, as a function of the input shock pressure. In this test an explosive wedge is impacted by a plane shock wave from an explosively-driven plate, usually brass.



The velocity of the transmitted shock wave, as the wave advances through the explosive wedge, is obtained as a function of the distance travelled by the shock through the wedge. From this set of data a large amount of information can be inferred concerning the behavior of the test explosive specimen. For example, one can determine one point on the Hugoniot curve for the unreacted explosive from these measurements (12). More important, since one obtains a set of values of the velocity of the wave (in the wedge) as a function of its penetration into the wedge, one gets a detailed picture of how this shock builds up from a (presumably) inert shock into an accelerated shock, and (finally) into a steady-state detonation. Tables 9 and 10 contain the various data obtained from the wedge test.

Figure 2 shows a typical curve for the build-up to detonation in a 25° DATB wedge, along with curves for pressed and cast Comp B. The initial shock velocity in the DATB was 4750 m/sec. The amplitude of this shock was 76.5 kilobars. The outstanding feature of this curve is that the instantaneous shock velocity within the explosive rises 10 to 20% above the normal detonation velocity (7600 m/sec) before receding and stabilizing at the normal detonation

TABLE 9
Wedge Test Parameters for Pure DATE, TATB, and TNB

Shot Mo.	Brass Thick (cm)	Initial Shock Velocity H.E. (m/sec)	Initial Particle Velocity H.E. (m/sec)	Initial Shock Pressure H.E. (kb)	Initial Compression H.E. (V/V ₀)	ρ_0 H.E. (g/cm ³)	D (Final) (m/sec)
DATE							
1	1.27	4670	1167	99.2	0.750	1.820	7640
2	1.27	4660	1167	99.3	0.750	1.825	7460
3	2.54	4870	972	85.4	0.800	1.803	7620
4	2.54	4700	979	82.8	0.792	1.799	7700
5	3.81	4736	892	76.6	0.810	1.813	7590
6	3.81	4767	892	76.5	0.815	1.810	7500
TATB							
1	2.54	4612	976	83.7	0.788	1.862	Failed to Detonate
2	1.27	5140	1140	109.1	0.778	1.862	
3	1.27	5200	1129	109.3	0.783	1.863	
4*	1.27	5200	1129	106.0	0.783	1.800	6200
TNB	1.27	Only Reactive Shock Was Observed					6400

* 30-degree wedge, maximum thickness 3.10-cm.

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TABLE 10
Wedge Test Parameters for Fiastic-Bonded Compositions of DATB and TNA

Shot No.	Brass Thick (cm)	Initial Shock Velocity H.E. (m/sec)	Initial Particle Velocity H.E. (m/sec)	Initial Shock Pressure H.E. (kb)	Initial Compression H.E. (V/V) ₀	ρ_0 H.E. (g/cm ³)	D (m/sec)
DATB/BRL 2741 (95/5)							
1*	1.27	4820	1154	99.4	0.759	1.77	7350
2	2.34	4720	982	82.0	0.792	1.77	Failed to Detonate
DATB/EPON (95/5)							
1	2.54	5120	971	96.0	0.810	1.73	7350
TNA/Zytel (95/5)							
1	2.54	4780	993	77.7	0.792	1.637	7200
2	3.81	4698	909	70.5	0.822	1.650	7400

* 32-degree wedge, maximum thickness 3.10-cm.

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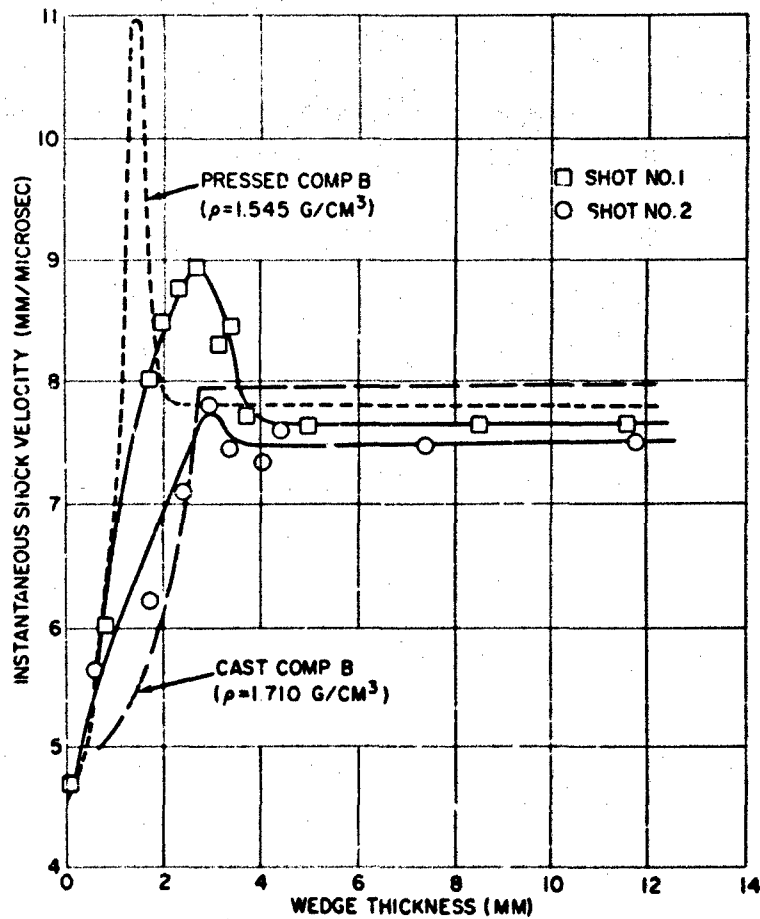


FIG. 2 INSTANTANEOUS SHOCK VELOCITIES IN DATB AS A FUNCTION OF SHOCK PENETRATION DEPTH COMPARED TO COMP B.

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velocity. A surprising result shown in this curve is that (other than the velocity "overshoot") the build-up in DATB is not too different from that of cast Composition B (12). This marked difference from its behavior in the impact hammer test shows that the sensitivity of DATB to mechanical shocks is strongly dependent on the rate of shock loading.

TATB at an initial density of 1.86 g/cm^3 when formed into a 25° wedge (maximum thickness 1.3 cm) did not produce an accelerating shock wave which built up to detonation even though a pressure of 109 kb was transmitted to the wedge. However, when a 32° wedge (maximum thickness 3.1 cm) was used to provide a longer shock run, and the initial shock pressure transmitted to the wedge was 106 kb, a pronounced velocity overshoot reaching 11,000 m/sec occurred after the shock had penetrated 1.0 cm into the wedge. In contrast to the velocity overshoots noted in the DATB results with 25° wedges, this shock wave did not settle to 7900 m/sec, the normal detonation velocity of TATB at 1.86 g/cm^3 . Instead the wave velocity receded to a steady value of only 6200 m/sec for the remaining wedge thickness.

Wedges of suitable quality were not easily machined from high density pellets of picramide and trinitrobenzene because the pellets tended to fall apart during machining. By replacing the wedge (in the wedge test) with cylindrical pellets of various thicknesses, build-up-to-detonation data, analogous to that of the wedge test were obtained. When picramide pellets, 1 to 5-mm thick were subjected to a transmitted shock of 90 kb an initial (inert) shock wave developed having a velocity of 5000 m/sec. High velocity detonation was obtained in pellets 3 to 4 mm thick as evidenced by the appearance of luminous product gases in the camera record. In wedge tests of picramide, plastic-bonded with zytel (95/5), velocity overshoots exceeding 8500 m/sec were observed (Figure 3). The data points for these curves were obtained by subjecting 30-degree wedges to transmitted pressures of 77.7 and 70.5 kb.

In 3 to 10-mm thick trinitrobenzene pellets of density 1.69 g/cm^3 , shocked to about 90 kb, an initial instantaneous shock wave velocity of 6800 m/sec was obtained. Since this velocity was just 200 m/sec less than the normal detonation velocity obtained for 5.1-cm diameter TNB, we conclude that the 3-mm pellets of TNB were initiated to full detonation within a thickness less than 1-mm by the 90 kb shock.

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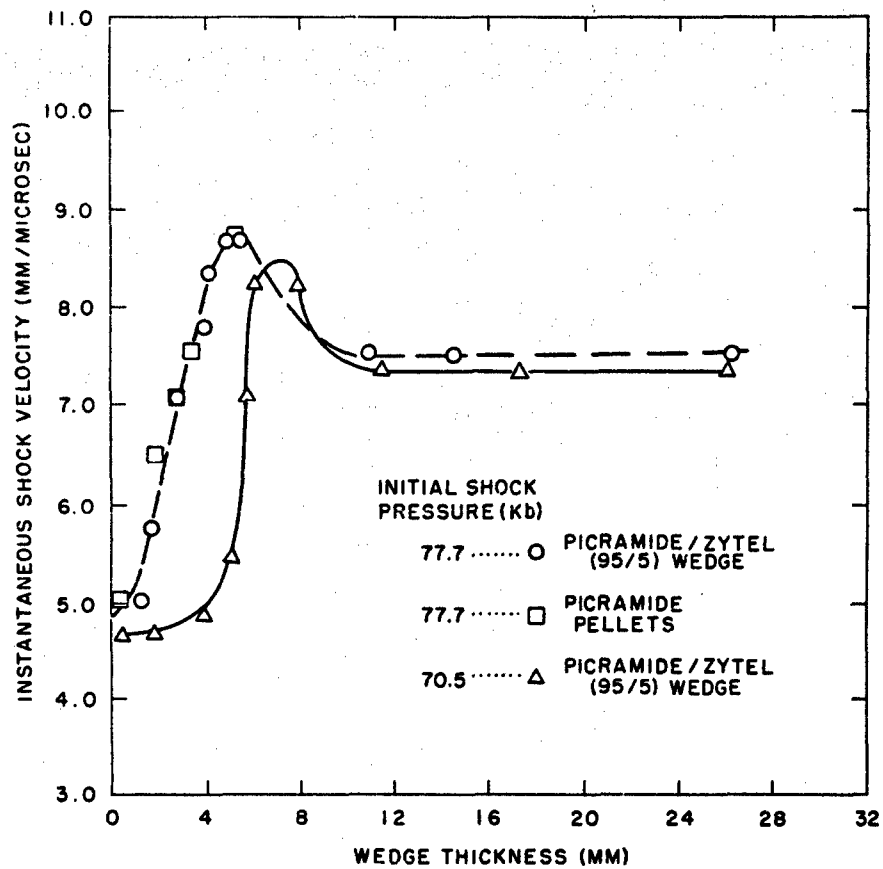


FIG. 3 INSTANTANEOUS SHOCK VELOCITIES AS A FUNCTION OF SHOCK PENETRATION DEPTH FOR PICRAMIDE / ZYTEL (95/5)

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The wedge test data for the above compounds are listed in Table 9. Table 10 contains the data for some of these compounds, plastic-bonded with various binders:

DATB/BRL 2741* (95/5), DATB/EPON** (95/5), and TNA/Zytel*** (95/5).

When a 25-degree wedge of DATB/BRL 2741, was shocked, the shock wave failed to build up to detonation even though the initial pressure developed within the wedge was 82 kb. On the other hand build-up-to-detonation (from an initial velocity of 5120 m/sec) with a 86 kb shock wave pressure was obtained with a standard 1.3-cm high, 25-degree wedge of DATB/EPON 1001 (95/5). (This difference could be related to the difference in behavior between the two plastics.) When the shock run for the DATB/BRL 2741 was increased to 3.1 cm (using a 30-degree wedge), and the transmitted pressure increased to 100 kb, a smooth build-up-to-detonation was obtained.

7. CONCLUSIONS

7.1 Detonation Properties. The steady state detonation parameters of TNA, TNB, DATB and TATB are insensitive to the number of amino groups.

The detonation velocity-charge density relationship $D = 2480 + 2852 \rho$ (g/cm^3), and measured detonation energy of 81.5 ± 15 cal/g are the same for each series member.

Detonation velocities of TNA, TNB, DATB, and TATB at loading densities of $1.6 \text{ g}/\text{cm}^3$ are predicted within 2% by the hydrodynamic theory, using the HKW equation of state.

At charge densities of $1.80 \text{ g}/\text{cm}^3$, the measured detonation pressures of DATB and TATB are 251.0 kb and 259.4 kb respectively. A detonation pressure of 174.6 kb was measured for TATB at $1.50 \text{ g}/\text{cm}^3$. At $1.64 \text{ g}/\text{cm}^3$ a detonation pressure of 219.2 kb was measured for TNB.

7.2 Sensitivity. The shock sensitivity and failure diameter, are functions of the number of amino groups, heats of formation and oxygen balance. From the most sensitive to shocks, to the least sensitive, both the heat of formation and oxygen balance increase as one goes from TNB to TNA, DATB, and TATB; i.e. as the number of NH_2 groups increases. TNA gave detonation failures at diameter about 0.3-cm; DATB and TATB fail at 0.53-cm and 1.3-cm diameters respectively.

*BRL 2741 (Phenolic Resin), The Bakelite Corporation, New York City, New York.

**EPON (Epoxy Resin); Shell Epon 1001; Shell Chemical Company, Emeryville, California.

***Nylon, trade name.

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The sensitivity of these compounds to mechanical shocks, as exhibited in the NOL wedge test, decreases as the number of NH_2 -groups increases. Thus even though a 100 kb pressure developed within the wedge, TATB failed to detonate. However under the same shock pressure normal detonation was developed in 1.8 mm by DATB and even less than 1.8 mm by both TNA and TNB.

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APPENDIX A THERMO-HYDRODYNAMIC THEORY OF DETONATION

The properties of detonation waves in solid explosives have been studied by various investigators (33, 34, 35, 36) using the Halford-Kistiakowsky-Wilson equation of state,

$$P (V_m - \eta V_s) = \frac{n_g R T}{M} (1 + X e^{BX}), \quad (A1)$$

$$X = \frac{K}{M} (V_m - \eta V_s) T^\alpha, \quad (A2)$$

$$\alpha = 1/4,$$

$$B = 3/10.$$

V_m and V_s are the specific volumes of the gas-solid mixture and of the solid respectively. η is the weight fraction of the solid, and n_g is the number of moles of product gases per M grams of the mixture. K is the empirical covolume parameter of the i -th gas and is a summation made over all gas species present.

In a detonation, the chemical energy released is equal to difference between the internal energy of the products and of the initial materials. The expression for M grams of explosive, assuming the incompressibility of solid products is

$$E(V, T) - E(V_c, T_0) = n_g \bar{c}_V (T - T_0) + \int_{T_0}^T \left(\frac{\partial E}{\partial V} \right) dV + Q, \quad (A3)$$

and in terms of the Halford-Kistiakowsky-Wilson equation of state,

$$\int_{T_0}^T \left(\frac{\partial E}{\partial V} \right) dV = n_g RT \alpha X e^{BX}. \quad (A4)$$

The mean ideal heat capacity, $\bar{c}_V$, in cal/mole/°K at constant volume for each decomposition V product is given by

$$\bar{c}_V = \frac{1}{T - T_0} \int_{T_0}^T c_V dT. \quad (A5)$$

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$$\bar{c}_v = A + BT, \quad (A6)$$

where $A = \sum n_i A_i$; $B = \sum n_i B_i$ are constants. The heat of reaction per mole is

$$Q = HFE - \sum n_i HF_i - n_g RT_o. \quad (A7)$$

HFE is the heat of formation of the explosive $\sum n_i HF_i$ is the sum of the individual molar heats of formation of the decomposition products and n_g is the number of moles of product gases. The last term in Equation (A7) is the difference between the reaction carried out at constant pressure and constant volume, assuming ideal behavior of the product gases.

The Rankine-Hugoniot equation for a reacting shock wave is

$$E(V, T) - E(V_o, T_o) = 1/2 (P + P_o) (V_o - V). \quad (A8)$$

If $P \gg P_o$ and $T_o = 300^\circ K$ (where the zero subscript refers to conditions ahead of the reactive shock (detonation), and the expressions for C_v and the HKW equation of state are used, the Rankine-Hugoniot becomes a quadratic in T ,

$$BT^2 + T(A - B \cdot 300^\circ K - n_g R) - Q - A \cdot 300^\circ K = 0, \quad (A9)$$

where

$$\dagger = \frac{R P(x)}{2} \left(\frac{V_o - 1}{V - \eta V_o} \right) - I(x), \quad (A10)$$

$$I(x) = n_g R \alpha X e^{BX}, \quad (A11)$$

and

$$P(x) = 1 + X e^{BX}. \quad (A12)$$

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(Various I-functions have been tabulated and an iterative procedure developed by Snay (35, 39) for their use in detonation calculations.)

The internal energy of the products in the detonation wave is a function of either T and V or of P and V. If P and V are to be determined individually a second relation is required. This is furnished by the equation

$$\left(\frac{\partial P}{\partial V} \right)_{\text{Hug.}} = - \frac{P_{\text{CJ}}}{V_0 - V_{\text{CJ}}} \quad (\text{A13})$$

which is derived from the Chapman-Jouquet condition,

$$D = u + C \quad (\text{A14})$$

D is the detonation velocity, u, the particle velocity, and C, the velocity of sound at the front. $\left(\frac{\partial P}{\partial V} \right)_{\text{Hug.}}$ is the gradient

of the line in the P-V diagram which represents the Rankine-Hugoniot equation. If the identity and total number of moles of product gases are fixed by an assumed decomposition equation for the explosive at a given loading density, Equation (A9) may be solved for T for each value of X. The pressure and volume for each value of X and T are calculated from the equation of state. When a number of P-V points have been obtained in this way, the Hugoniot curve can be drawn. The tangent drawn to the curve from the point on the line $P = 0$ at which $V = V_0$, determines the detonation velocity of the explosive, and the pressure and specific volume in the Chapman-Jouquet plane.

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SUBJECT ANALYSIS OF REPORT

SUBJECT ANALYSIS OF REPORT			
DESCRIPTORS	CODES	DESCRIPTORS	CODES
Explosion	EXPS	Aniline	ANIL
Symmetrical	SYM	Diamino	DIAM
Tinitro	TRIT	Groups	GOUP
Benzene	BENZ	Heat	HEAT
Amino	AMIN	Formation	FORM
Substituted	SUBT	Oxygen	OXYG
Shock	SHOC	Balance	BALN
Sensitivity	SENV	Mechanical	MECA
Failure	FAIL	Detonation	DETO
Diameter	DMET	Pressure	PRES
Tetra	TERA	Velocity	VELC
Nitro	NIRO	Measurements	MEAU

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1. Naval Ordnance Laboratory, White Oak, Md. (NOL technical report 61-81) THE EXPLOSIVE PROPERTIES OF THE AMINO-SUBSTITUTED, SYMMETRICAL TRINITROBENZENES (U), by N. L. Coleburn and B. E. Drimmer. May 1963. v.p. BuWep task RUMS 4E OOC/212-1/FOO8-10-004. CONFIDENTIAL The shock sensitivity and failure diameter of 1,3,5 - trinitrobenzene (TNB), 1 - amino 2,4,6 - trinitrobenzene (TNA), 1,3 - diamino 2,4,6 - trinitrobenzene (TATB) are functions of the number of amino groups, heats of formation and oxygen balance. TNB is the most sensitive to mechanical shocks. As the number of amino groups increase the detonation failure diameters increase.	1. 1,3,5-Trinitrobenzene 2. 1-amino 2,4,6-trinitrobenzene 3. 1,3-diamino 2,4,6-trinitrobenzene 4. Explosives - Sensitivity I. Title II. Coleburn, Nathaniel L. III. Drimmer, Bernard E., Jr. author IV. Project	1. 1,3,5-Trinitrobenzene 2. 1-amino 2,4,6-trinitrobenzene 3. 1,3-diamino 2,4,6-trinitrobenzene 4. Explosives - Sensitivity I. Title II. Coleburn, Nathaniel L. III. Drimmer, Bernard E., Jr. author IV. Project	Abstract card is Unclassified
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