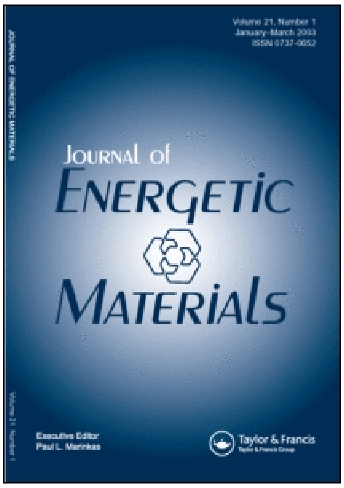

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Stability tests of TNAZ — thermal and shock impact

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STABILITY TESTS OF TNAZ --- THERMAL AND SHOCK IMPACT

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ABSTRACT

Two types of tests were performed on 1,3,3-trinitroazetidine. (A) Analyses were made of decomposition products generated from gaseous TNAZ when kept in stainless steel or Pyrex containers at various temperatures (< 240°C) for up to 24 hours. (B) Evidence for evaporation of the compound or the appearance of NO_2 was sought when thin layers of solid TNAZ (initially at R.T.) were impacted by shock-waves, in an Ar or Ar/O_2 medium. The step functions of the pressure/temperature increments had rise times well below microseconds. The pressure jumps ranged from 2-10 atm, and the associated temperature jumps varied from 550 to 2500K. In all these tests the elevated pressure/temperature conditions lasted for 1.5 ms. Finally, shock-waves were impacted on a well packed cavity (3/16" thick; 3/8" diameter) filled with powdered TNAZ to a

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depth of 1/8". Under these relatively mild perturbations no detectable evaporation or decomposition was observed.

INTRODUCTION

1,3,3 trinitro-azetidine is a member of a new generation of high energy explosives/propellants[1]. It is relatively insensitive to impact. Its thermal stability above the melting point (101°C) is particularly attractive because it permits safe casting. Over the past few years several investigators undertook to determine its chemical behavior upon subjecting samples, in the solid state[2], or in solutions of benzene and other solvents[3], or in the gas phase in molecular beams[4] to elevated temperatures. The pyrolysis of gaseous TNAZ (highly diluted in Ar) induced by shock heating is currently being investigated in this laboratory, with emphasis on the determination of the fragmentation sequence during the early stages of decomposition. In conjunction with that study we here report experimental results on the vulnerability of gaseous TNAZ to surface conditions, and on the effect of shock impacts on solid films or packed powder.

EXPERIMENTAL SECTION

(A) 1,3,3,-trinitro-azetidine was obtained from U.S. Army Armament Research, Development and Engineering Center, Picatinny

Arsenal. Gaseous TNAZ-Ar mixtures were prepared by first introducing a weighed amount of the solid into a small container that was filled with Ar at room temperature. The container was pumped down to <10^{-3} torr and then refilled with Ar to ~ 2 atm. The flask was placed in the an oven and gradually heated to ~ 110°C to allow the solid TNAZ to melt and evaporate. The oven temperature was then raised to the desired temperature and kept at that temperature for 6 - 24 hours before analysis. The gas mixture was cooled to room temperature and analyzed by GC (HP 5720A) on a Sulpelco Porapack Q stainless steel column, using a thermal conductivity detector, or by FTIR. The presence of CO and NO demonstrated that the TNAZ had decomposed.

The aim of this series of tests was to determine the upper temperature at which TNAZ may be kept without decomposition. Two types of containers were used. One was of stainless steel (300 ml) and the other of Pyrex (500 ml). In each case 4 mg of the solid (eventually diluted when gaseous, to 0.09% in Ar) was introduced into the container before it was placed in the oven. In stainless steel, when kept for ~ 20 hrs at 110°C, considerable CO and NO was produced. About twice that much of these gases was generated when kept at 150°C for the same period. In contrast, in a Pyrex vessel, no CO nor NO was found. Only when the temperature was raised to ~ 200°C for 13 hrs was decomposition noted. The products, all in the gas phase in the cooled mixture, when analyzed by FTIR, consisted of $NO > CO > HCN > NO_2 > H_2CO > CO_2$ and traces of other species. The distribution of products is essentially identical to that generated upon shock heating (750-1100K with residence time of 1.5 ms) of TNAZ-Ar mixtures, indicating that the decomposition sequences for the two pyrolyses are similar. It should be noted that the initial decomposition temperature we noted is somewhat lower than that reported by Iyer et al.[5] (240°C) but is higher than that found by Brill et al.[2], who observed pyrolysis of TNAZ in a rapidly heated IR cell at 130°C. These discrepancies are most likely due to different types of surfaces of the containers. Indeed, we conclude that it is inadvisable to store TNAZ in steel containers when there is a potential for an excursion to temperatures above its melting point. Plastic or glass-lined containers are preferable.

(B) A 2.54 cm ID stainless steel shock tube was used to explore the effects of shock impacts on thin films of solid TNAZ. The driver section (120 cm long) was filled with He to pressures 30 - 120 psig, and the driven section (170 cm long) was filled either with high purity Ar or with a mixture of Ar(80%)-O_2(20%), variously to 20 - 650 Torr. Different thicknesses of Mylar diaphragms were used to generate controlled shock levels. The pertinent parameters for these experiments are best illustrated with an x-t diagram (Fig.1). When the incident shock-wave reaches the terminal plate, the gas immediately adjacent to the plate is compressed (step function) and heated, from P_1 (unshocked) to P_2, while the temperature rises from T_1 to T_2. Upon reflection from the end-plate,

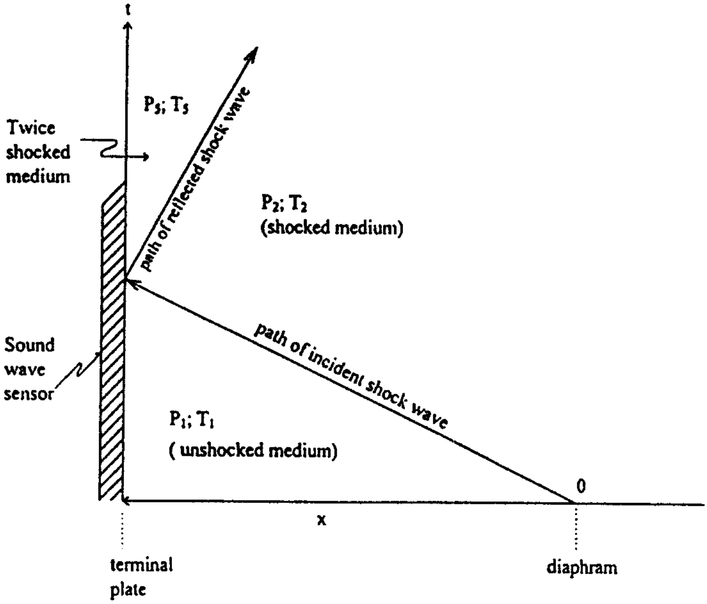

Figure 1. x-t diagram for shock impact experiments

the shock is reinforced so that the gas layer is additionally compressed from P_2 to P_5; T_2 to T_5. Typical magnitudes are listed in Table 1. The gas at the terminus of the shock tube is subjected to these increments within (estimated) time spans considerably less than microseconds. The elevated temperatures and pressures remain in the (essentially) stationary gas layer for about 1.5 ms prior to a reverse-flow induced by an expansion wave. In addition, a pressure sensor was attached to the external surface of the end plate, to record the arrival of the sound wave at that surface and the successive ringing within the end plate generated by the impact. The record was captured by an HP 54501 Digitizing

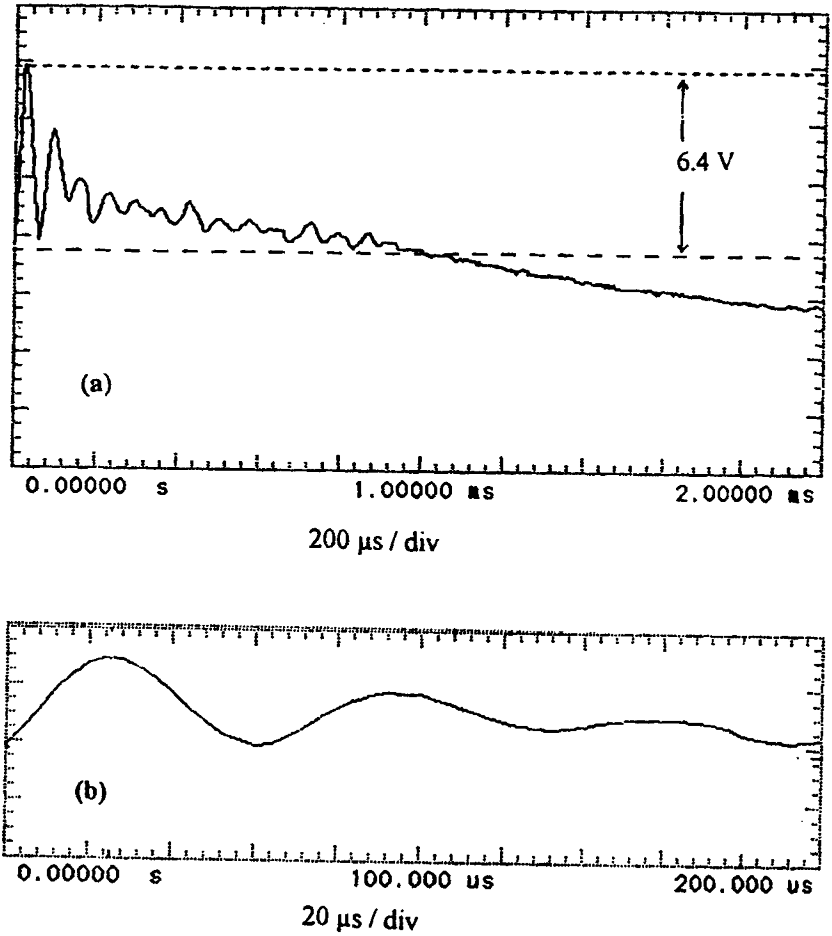

Figure 2. Typical piezo signal developed at the external surface of the end plate that shows arrival of the sound wave and ringing due to internal reflections. (a) 200 µs/large division; (b) 20 µs/large division.

oscilloscope (Fig. 2). The rise time of this signal was determined by the speed of the induced pressure wave in the terminal plate material and its thickness. Note that sound speed in aluminum is 6420m/s, while in polystyrene it is 2350m/s.

A thin layer of solid TNAZ was placed on the inner surface of the end plate. This film was prepared by placing a calculated number of drops of a 0.045M solution of TNAZ in acetone onto the

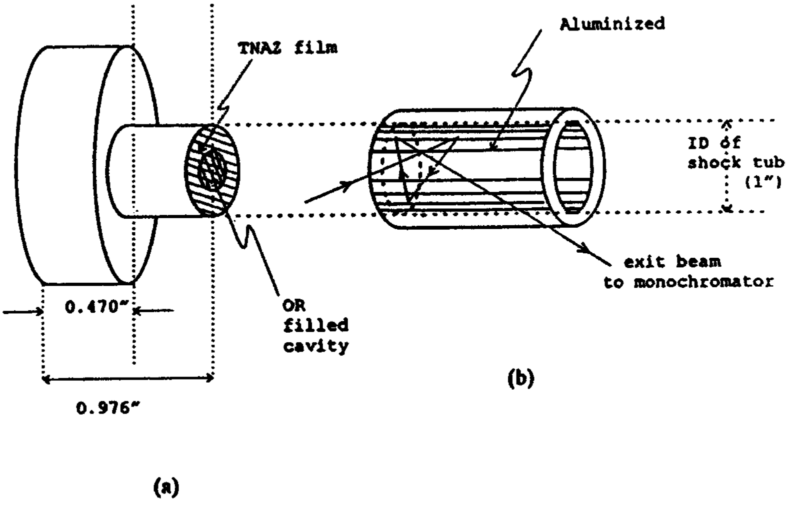

Figure 3. (a) End plate for sensitivity tests; (b) schematic of probe-beam internal reflection in the quartz-tube extension of the shock tube.

measured area of the end plate projection (Fig.3a) and allowing the solvent to evaporate. The estimated thicknesses of these films were 4×10^{-3} - 1.5×10^{-2} mm. Evaporation of the solid and/or its pyrolysis sequence was monitored by recording absorption in the gas phase of a UV probe beam directed within 1 mm of the film; at 271 nm(TNAZ) and 405 nm (NO_2). The radiation was the focused emission from an Oriel Xenon Arc lamp #6256, directed normal to the shock tube axis. This beam was internally reflected several times within the quartz tube extension of the shock tube, thus providing an effective path-length of about 16 cm. (Fig. 3b). Piezoelectric gauges, inserted near the end of the shock tube, separated by 10.00 cm, recorded shock passage times (to ± 1 μs), thus providing the data needed for calculating all the essential shock parameters.

To study the effect of pressure and temperature separately, P_1 (the pressure of the driven section) was kept at 590 torr for a sequence of rupture pressures of 30, 50, 70, 120 psig. The corresponding P_5 (pressure in the reflected shock wave) thus generated were from 3-10 atm (much too low to initiate reaction), and temperatures in the range 700-1000K (eventually reflected shock temperatures were raised to 4000K). Real time measurements of the appearance of gaseous TNAZ or NO_2 could be followed from their UV absorptions. No detectable amounts of either TNAZ or NO_2 were found in these experiments (Figure 4). The effect of high temperatures was tested by keeping P_1 at ~ 20 torr, using rupture pressures $>$100 psig. The highest temperature thus attained was ~ 2500K and

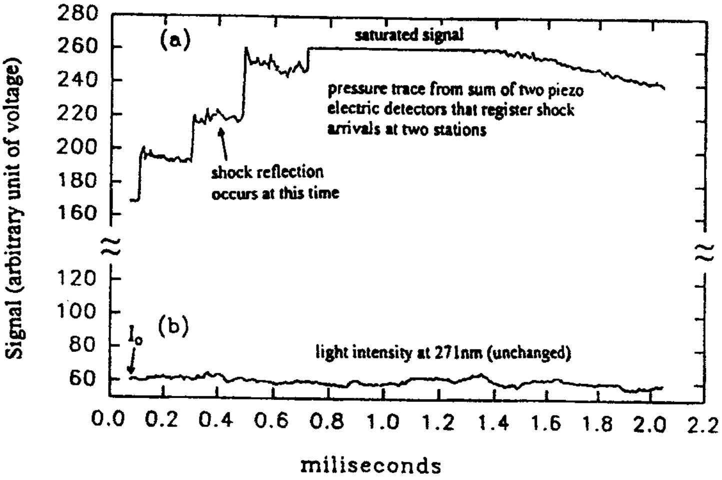

Figure 4. (a) Typical voltage trace of piezo-electric detectors of shock arrival times; (b) scan of phototube output signal, indicating that no UV absorption was generated.

the corresponding pressure ~ 1.5 atm. Again, no detectable gaseous TNAZ or NO_2 was generated.

End plates of different thermal conductivity (one of aluminum and another of plastic) were also tested in these experiments.

Table 1. Conditions of Shock Impact Experiments on Thin Films of TNAZ (thickness: 4.0 x 10^{-3} mm)

exp.#	λ(nm)	P_1(Torr)	P4(psig)	P_5(atm)	T_5(K)	$[NO_2]$(mol/l)	[TNAZ](mol/l)
7/8" Al end plate,1mm from probe light							
523	271	480	50	3.27	596	-	< 2e-6
524	271	480	70	4.35	683	-	< 2e-6
525	271	480	70	4.35	683	-	< 2e-6
526	271	480	70	3.51	708	-	< 2e-6
527	271	480	50	3.51	616	-	< 2e-6
528	271	480	20	7.08	875	-	< 2e-6
3/8" plastic end plate,4mm from probe light							
529	271	480	50	3.51	615	-	< 2e-6
530	271	480	75	4.68	708	-	< 2e-6
531	271	80	50	1.91	1148	-	< 2e-6
532	271	120	70	2.87	1148	-	< 2e-6
533	271	60	70	2.20	1500	-	< 2e-6
534	271	40	70	1.95	1804	-	< 2e-6
thickness of TNAZ film: 8.0x10^{-3} mm (driven section filled with 20% O_2 in Ar)							
535	271	62	65	1.76	1271	-	< 1e-6
536	271	70	70	2.07	1305	-	< 1e-6
537	405	70	70	1.98	1271	-	< 5e-6
thickness of TNAZ film: 1.5x10^{-2} mm							
538	271	60	70	3.93	2221	-	< 2e-6
539	271	60	110	3.22	1928	-	< 2e-6
540	271	20	110	1.53	2490	-	< 2e-6
541	271	30	110	2.18	2395	-	< 2e-6

Table 2. Conditions of Shock Impact Experiments on Thin Films of TNAZ (0.100" end plate, 10 mm from probe light; thickness of the TNAZ film: 1.0x10^{-2} mm)

exp.#	λ (nm)	P_1(Torr)	P_4(psig)	P_5(atm)	T_5(K)	[NO_2](mol/l)	[TNAZ](mol/l)
			0.100" plastic end plate				
544	271	100	50	2.29	1120	-	< 3e-6
545	271	100	70	5.11	1864	-	< 3e-6
547	271	100	120	4.23	1641	-	< 3e-6
548	271	10	120	2.07	2305	-	< 3e-6
			0.100" Al end plate				
556	271	590	38	3.49	559	< 3e-6	-
557	271	590	60	3.88	586	< 4e-6	-
558	271	590	80	5.16	671	< 4e-6	-
559	271	590	110	10.6	974	< 4e-6	-
560	271	40	50	1.35	1416	< 4e-6	-
561	271	46	70	2.04	1692	< 5e-6	-
562	271	46	108	2.72	2066	-	< 1e-6
563	405	48	102	2.70	1995	-	< 1e-6
564	405	46	70	1.94	1641	-	< 1e-6
565	405	40	50	1.51	1522	-	< 2e-6
			end plate shown in Fig 3a. Packed cavity (4.5 mm thick)				
566	405	50	110	2.72	1927	< 5e-6	-
567	405	590	110	7.32	791	< 4e-6	-
568	405	590	110	7.60	807	< 4e-6	-
569	405	590	110	7.05	776	< 4e-6	-

Visual inspection of the end plate after each shock indicated that the TNAZ film remained essentially intact, but it is probable that the solid did melt but re-solidified upon cooling by the supporting plate. The pressure jumps developed in these experiments were orders of magnitude too low to induce detonations. However the sharp rises in ambient gas temperature could have induced reactions. In Tables 1 and 2 the cited upper limits on [TNAZ] and [NO_2] should not be taken as estimates of the actual concentrations of these two species, rather they specify the limits of our spectroscopic detectivity.

The possibility that shock waves may induce propellant combustion was investigated by filing the driven section with 20% O_2-Ar mixture. The experimental results indicate that under our conditions such processes do not occur. The final tests were made with shock wave impacts on a cavity (3/16" deep; 3/8" diameter) filled with TNAZ powder, to a thickness of 4.5mm. A few drops of acetone were added to provide adhesion of the powder to the cavity. Shock conditions for these runs are listed in the lower part of Table 2. Again, no decomposition of TNAZ was detected within the sensitivity limits of the UV absorption probes.

COMMENTS

Theories of detonations of gaseous and solid fuels have been discussed extensively in the literature[6,7]. Theoretical studies by

Tarver et al.[8] suggested that when a solid explosive is subject to shock waves, hot spots may be generated. These hot spots can either detonate and hence cause large scale explosions or quickly cool by transferring heat to the surroundings. The outcome depends both on the strength of the shock wave (and its duration) and the chemical properties (chemical decomposition mechanism) of the explosive studied. The above tests demonstrate that the shock-wave temperatures and pressures developed in our shock-tube (Ar or Ar/O_2 medium) are not sufficient to develop critical hot spots in TNAZ.

The magnitudes of the impact pressures generated in our conventional shock-tube (~7.6 atm) are clearly insufficient to induce any significant conversions in TNAZ. Explosion driven pressure jumps of the order of 10 GPa (10^5 atm) for durations of a microsecond do cause decompositions in various organic compounds[9]. Changes in the UV and visible absorption spectra, concurrently with decomposition, were observed in nitromethane subjected to shock-wave pressures ~14 GPa[10]. Detonation product distributions were measured for PETN, RDX, HMX, HNS, TNT and TATB, induced in cylindrically shaped explosive charges[11]. It is interesting to note that in the latter experiments, as in our analyses of products developed during gas-phase shock heating of TNAZ highly diluted in Ar, the observed product distributions did not agree with predictions based on equilibrium assumptions[12].

For the anticipated effects on thin TNAZ layers of the high temperature gas generated at the terminal plate of the shock tube we present only qualitative estimates. These contrast with the reported changes in phase induced by intense shock waves in Ar; simulations of such experiments were reported by Belonoshko[13]. We calculate that for the TNAZ layers, as prepared, about one μmol/cm^2 was deposited on the terminal plate. The quoted heats of melting and sublimation are 1.8 and 15.1 kcal/mol[14]. Hence to induce such changes, assuming there is no significant heat loss to the back-plate during the 1.5 ms residence time, 1.8x10^{-3} cal (for melting) or 15.1x10^{-3} cal (for sublimation) would have to be transferred per ms from the gas layer to the TNAZ layer. That these magnitudes of heat transfer are more than satisfied, consider a reflected shock temperature T_5 = 2000K, and assume an efficiency of only 10% for conversion of the kinetic energy of the impinging Ar atoms into intermolecular vibrational energy in the TNAZ molecules on the surface. Then 160 cal/cm^2-s would be transferred; or 0.16 cal/cm^2-ms --- more than sufficient to induce both melting and sublimation. Our approximate estimates of the relaxation time for thermal equilibration of the returning, slightly cooled Ar atoms with the hot layers of shock-heated gas is in the sub-microsecond regime, so that no significant cold boundary layer develops during 1.5 ms. The fact that neither melting nor vaporization was observed indicates that both processes are kinetically limited. Conventional treatments of gas/solid heat transfer rates[15] do not address such short time processes.

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