

Stress-induced radical generation in TATB

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Degradation of polycrystalline TATB (2,4,6-trinitrobenzene 1,3,5-triamine) was studied using γ -irradiation, mechanical impact and frictional grinding. Evidence of molecular alterations were monitored using electron-spin resonance. Optical microscopy and electron scanning microscopy were used to observe changes due to mechanically working the powdered TATB. The dominant free radicals observed appear to be secondary radicals known to be stable at room temperature. This is an example where mechanical and photon generation produce the same final state free radical species.

1. Introduction

It has been proposed that free radical production may play an important role in mechanical detonation and that the stability of the radicals may be related to explosive sensitivity [1-3]. This paper explores the mechanical generation of free radicals and a preliminary search for highly reactive free radicals in TATB (2,4,6-trinitrobenzene-1,3,5-triamine). TATB is a very insensitive explosive to mechanical and thermal initiation [4, 5]. On the other hand TATB is readily degraded by ambient room light during handling as well as by X-ray and γ -ray irradiations [6]. A darkening of the TATB crystal from yellow to, eventually, black accompanies this degradation. It has been shown that free radical formation accompanies this colour change [6]. A nearly symmetric singlet electron spin resonance (ESR) signal at $g = 2.00234$ with a peak-to-peak width of 4.6 gauss was reported by Britt *et al.* [6]. Extraction of heavily photolysed mixtures of TATB with dimethyl sulphoxide produced dissolved free radicals showing resolved hyperfine splittings. Britt and co-workers [6] suggested that this dissolved species is the TATB-H adduct (hydrogen coupled to the NO_2 groups). In this study TATB samples from two different sources were studied. The first was obtained from

R. Reed of China Lake Naval Research Laboratory at China Lake, California. The second provided by W. Moniz and A. D. Britt of the Naval Research Laboratory in Washington, DC was reportedly very nearly chlorine free. This latter material (shown in the micrograph of Fig. 1a) was composed mostly of very small particles, i.e. $< 5 \mu\text{m}$, while the former (shown in the micrograph of Fig. 2a) was composed of much larger particles, i.e. $> 50 \mu\text{m}$.

2. Experimental procedure

The TATB powder was sealed in evacuated quartz tubes. These tubes were then immersed in liquid nitrogen and irradiated with γ -rays from a 5050 Curie caesium source. The TATB powder was radiated up to 10 Megarads to accumulate frozen-in concentrations of gamma-ray-produced free radicals. After irradiation, the sample end of the quartz tube was immersed in a small nitrogen dewar so that the protruding sample-free end of the quartz tube could be heated with a torch. This heating completely removed the γ -ray induced quartz colour centres with their associated ESR spectrum, from the heated end of the quartz. The quartz tube with the sample was then immersed in a larger liquid nitrogen bath and after recooling to liquid nitrogen temperature, inverted, allowing

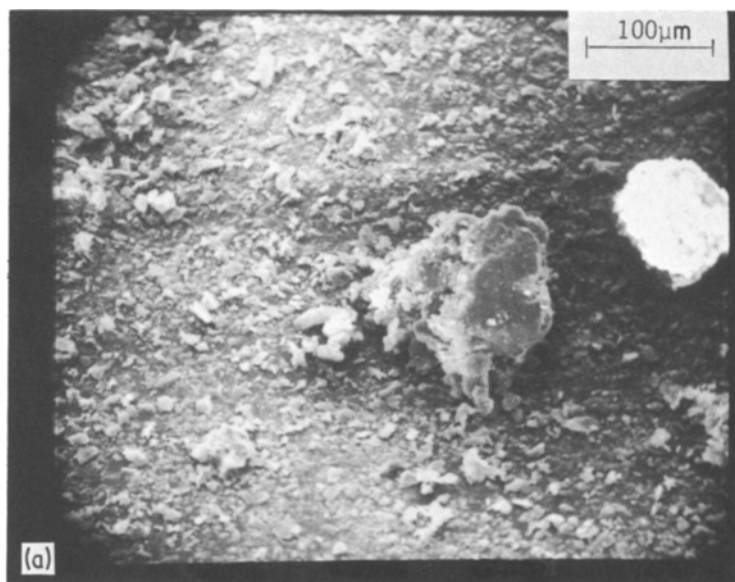
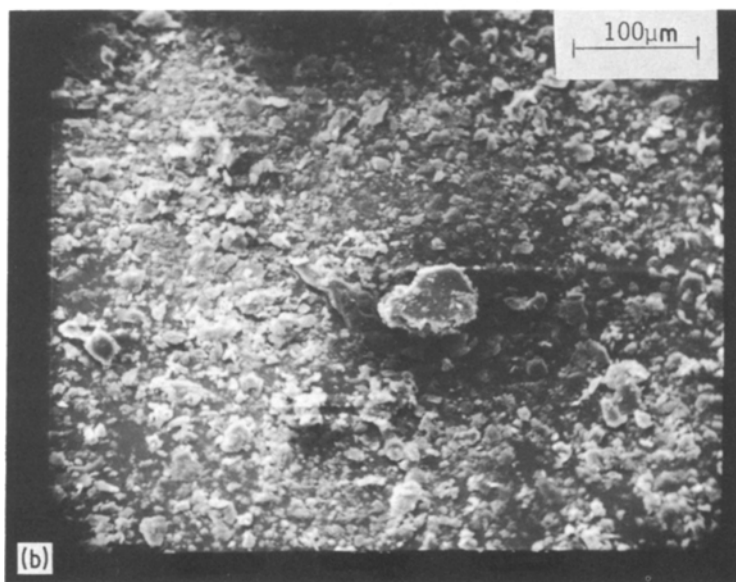


Fig. 1 (a) "Micronized" chlorine-free TATB as-received and (b) after grinding.

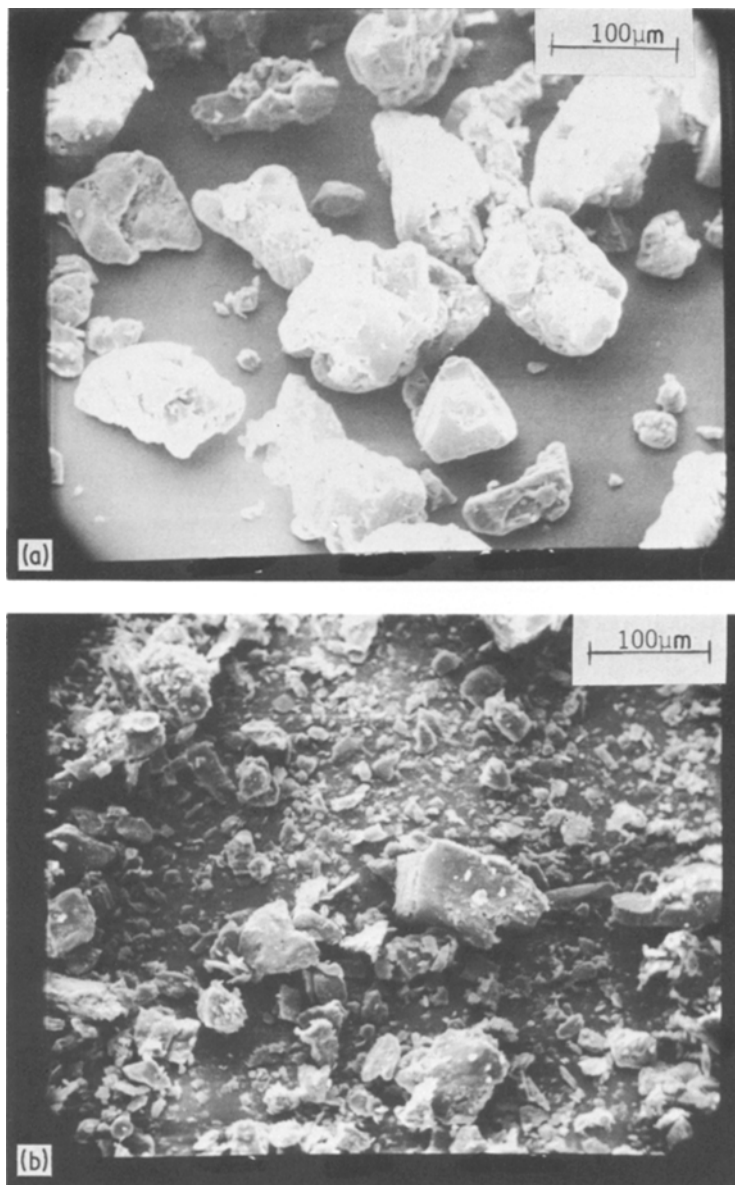


the powdered sample to slide down to the colour centre free end of the quartz tube. The quartz tube containing the sample was then quickly inserted into a precooled low temperature accessory in the microwave cavity of the ESR spectrometer. Temperature control was achieved using a Varian E-4540 variable temperature controller. Measurements were usually performed at -150°C . Measurements on occasions were performed in a minimum of time after cessation of γ -irradiation. The time from cessation of irradiation to completion of an electron-spin resonance scan could be reduced to ten minutes. This combination of

keeping the sample cold and performing the measurements with minimum of time delay maximizes the likelihood of detecting reactive unstable radicals.

Mechanical stress was applied to the polycrystalline TATB in two quite different manners. We first applied mechanical stresses from frictional grinding TATB powders in a standard alumina mortar with a pestle. We first performed this grinding near liquid nitrogen temperature. A smaller mortar was placed inside a larger mortar. Liquid nitrogen was poured into the larger mortar cooling the smaller mortar containing the TATB

Fig. 2 (a) Normal TATB as-received and (b) after grinding.



polycrystalline powder. The pestle was also cooled by immersing it into liquid nitrogen. The TATB powder was ground for a few minutes. The cold grindings were then transferred to a liquid nitrogen cooled quartz tube and this tube was then inserted into the precooled microwave cavity maintained at -150°C . To minimize the effect of room illumination on free radical concentration increases, the ESR measurements, grinding, weighing and handling were all done in a darkened room. A control sample held in the same room but not ground was periodically used to monitor radical increases due to the necessary handling operations.

The procedure here was to start with about 1 cm of TATB length in two quartz tubes. Both samples were measured for residual free radical concentrations. One sample became the control. The control TATB material was emptied into the mortar but not ground. Every handling and weighing operation of the control duplicated that for the ground sample except for the grinding operation. Usually more of the sample material was lost during grinding and transfer for the grinding sample than for the control. This posed no real problem, however, since the sample tubes and contents were always carefully weighed before

spectroscopic study and the concentrations determined from the actual weight of material present in the ESR cavity.

Since the residual radicals present were known to be very stable, grindings were also performed at room temperature. Experimentally this was much easier. Some TATB grindings were reground to see if the radical concentration continued to increase.

We received some TATB powder in which it was very difficult to produce additional radicals by grinding. Optical and electron microscope investigation on this TATB powder revealed it to be very fine in comparison to the previous TATB powder that consistently produced radical increases upon frictional grinding.

In addition to the grinding studies, impact of TATB and mixtures of TATB-HMX were performed using a small picatinny type drop hammer. With this drop hammer it is possible to impact onto liquid-nitrogen cooled samples as well as the normal room temperature impact.

3. Experimental results

Gamma-irradiated TATB showed the nearly symmetric singlet previously reported [6]. Efforts to detect more reactive radicals in TATB have so far been unsuccessful. The NO₂ radical commonly observed in irradiated HMX (cyclotetramethylene tetranitramine), RDX (cyclotrimethylene trinitramine), and PETN (pentaerythritol tetranitrate) [7, 8] is not easily observed in TATB. However, in γ -irradiated TATB a transient signal was observed that was believed to be an NO₂ triplet. To date, our efforts to consistently obtain the triplet-looking EPR signal or to make this signal comparable in strength to the dominant singlet have been unsuccessful.

The low temperature mortar and pestle grinding results are summarized in Table I which gives relative ESR signal strength for the residual radical concentration, the mechanically degraded TATB, and their differences. These numbers times 1.3×10^{14} gives an estimate of radical concentrations per gram of TATB. Table I shows some

TABLE I Summary of the low temperature mortar and pestle grinding results

Sample number	Residual	Grindings	Increase
1	2.46	4.96	2.5
2	10.2	15.2	5.0

TABLE II Summary of room temperature results

Sample number	Relative signal strengths	Increase	Sample treatment
3	1.49		Residual control
	2.22	0.73	First grindings
	3.22	1.00	Second grindings
	5.19	1.97	Third grindings
4	1.47		Residual control
	1.43		Weighed control
	2.42	0.99	First grindings
5	1.42		Control
	1.40		Weighed control
	1.77	0.37	Control from mortar
	2.01	0.24	Reweighed control
6	0.88		Residual
	1.42	0.54	First grindings
7	12.74		Residual
	18.2	5.46	Impacted twice with 0.5 kg m ⁻¹ with steel ball

representative results of low temperature grindings on TATB demonstrating a rather pronounced increase in radical concentration by mechanical work.

Table II summarizes the room temperature results.

Table III shows some representative results on the small particle size, chlorine-free TATB. Repeated efforts at grinding this material using the mortar and pestle produced small variations around the residual measurements. However, use of a picatinny-type drop hammer on room temperature TATB and liquid nitrogen cooled TATB produced a definite radical increase. An eight pound weight was dropped from the height indicated. This weight typically impacted approximately 40 mg of material and the effective area of impact was approximately 0.3 cm².

Since we found that the results were different for the different TATB samples that were provided for our work, we conducted a scanning electron

TABLE III Some representative results on the small particle size, chlorine-free TATB

Sample number	Relative signal strengths	Increase	Sample treatment
8	0.467		Residual
9	0.525	0.06	Cold grinding
10	2.28	1.81	Impact 18 inches, RT
11	1.17	0.70	Impact 18 inches, RT
12	5.16	4.69	Impact 28 inches, RT
13	2.75	2.28	Impact 28 inches, LN

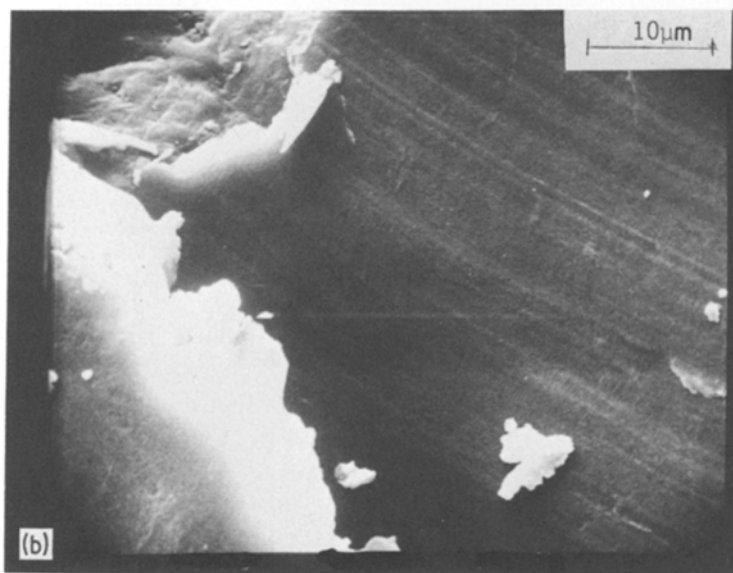
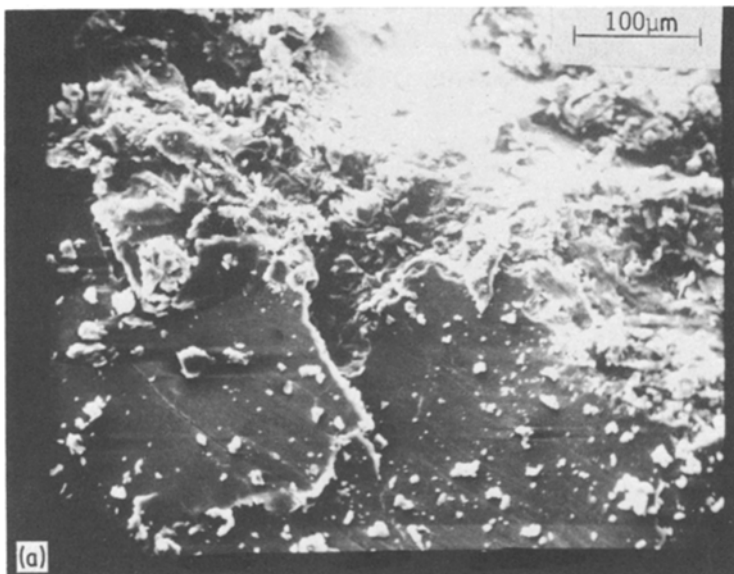


Fig. 3 Impacted "micronized" chlorine-free TATB.

microscope study. The inert or grinding insensitive TATB showed small grain size with little grain size change resulting from grinding. This TATB may be very similar to the micronized chlorine-free TATB described by Rizzo *et al.* [9]. The TATB that was sensitive to the frictional grinding operation had a lot of particles in the 100 μm range and showed considerable particle size reduction after grinding. Fig. 1 shows the before and after scanning electron micrographs for the TATB in which grinding did not produce a significant ESR spectra. Fig. 2 shows the before and after scanning electron micrographs for the grinding sensitive TATB.

The "micronized" TATB did show sizeable radical increase upon impact. Scanning electron micrographs reveal compact or fusing of the small TATB particles into large masses having smooth surfaces. Little if any evidence of grain structure was observed for this material with either optical or scanning electron microscopy. Fig. 3 shows SEM micrographs of the recovered impacted TATB at $\times 172$ and $\times 1729$.

4. Conclusions

It has been demonstrated that free radicals can be generated by mechanical stress in TATB. The degradation of the TATB molecule by stress or

by energetic photons produces the same final state free radical. This radical is relatively stable and inert at room temperature. Storage in the dark at room temperature for a month did not produce any detectable decay in the ESR signal consistent with the observations of Britt *et al.* [10]. Attempts to capture more reactive radicals in TATB at liquid nitrogen temperature have to date been unsuccessful.

The difference between the low temperature and room temperature grinding and impact response might be attributed to at least two causes. First the radicals, once formed, would be expected to be more stable at low temperatures and hence the same amount of molecular damage would probably result in more apparent free radicals. Secondly, low temperatures would be expected to modify the mechanical properties of the TATB and make it more brittle. As a consequence mechanically working would result in more fracture and associated free radical production. In light of the stability of the observed free radical in TATB at room temperature we feel that the latter explanation is the more reasonable.

However, both grinding and impact are difficult to control quantitatively even if one had uniform particle sized TATB. Hence our impressions from the data reported here favour low temperature grinding as the more efficient generator of radicals. There is too much scatter in the impact results to evaluate low temperature against room temperature impact. Both low and room temperature impacts produced sizeable increases in radical concentrations in TATB.

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