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ELECTRON SPIN RESONANCE STUDIES OF FREE RADICALS IN ENERGETIC M--ETC(U)
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2 ELECTRON SPIN RESONANCE STUDIES OF FREE RADICALS IN ENERGETIC MATERIALS

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The radicals generated by irradiation of nitroguanidine, and by irradiation, grinding and impact of HMX in polymeric binders were examined by ESR at several temperatures. The radiation sources were variously UV, electron beams, and gamma rays.

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ELECTRON SPIN RESONANCE STUDIES OF
FREE RADICALS IN ENERGETIC MATERIALS

Summary

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Upon UV irradiation triaminotrinitrobenzene (TATB) forms free radicals which are thermally stable to at least 220°C. At 300°C they decay with a half-life of 20 minutes to a second radical having a half-life of ca 55 minutes at 300°C. The ESR spectrum of each radical consists of a single line lacking discernible splitting. The structures of these radicals have not yet been established.

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I. Reactions between fracture-induced free radicals and energetic materials.

The fracture of nylon 6 produces two types of free radicals: initial free radicals which are the direct result of bond rupture and secondary free radicals which are the reaction and decay products of initial free radicals. It was expected that high speed ESR would be capable of characterizing this sequence of radicals. It was determined, however, that in the temperature regime of interest (near room temperature), the radical sequence is over before the mechanical vibrations in the system are damped. Thus, although in principal the high speed ESR system is capable of following the fast radical sequence, the vibrations incapacitate it during the critical period.

As an alternative to direct measurement of the short-lived initial free radicals, chemical interception, or spin trapping, was tried. Our experiments utilized research grade nylon 6, comparing the effects of selected coatings on ESR spectra. The most important comparison, for our purposes, is between samples coated before and after fracture. These are referred to as pre-coating and post-coating experiments, respectively. Pre-coating experiments permit reaction with both primary and secondary free radicals; post-coating experiments permit reaction only with secondary free radicals. This is due to the fact that primary free radicals in nylon 6 completely decay in milliseconds at room temperature. Samples were stressed at 25°C in a nitrogen atmosphere, but no special precautions were taken to remove

residual traces of oxygen. The results are shown in Figure 1 and Table 1.

The top spectrum in Figure 1 is obtained when picric acid (trinitrophenol) is coated on nylon 6 prior to fracture; the bottom spectrum is nylon 6 only, for comparison. It is evident that a major free radical reaction has occurred with picric acid. Further, coating picric acid onto the fibers after fracture causes no change in the bottom spectrum whatsoever. The interaction is, therefore, with primary free radicals only.

The decay in air (25°C) of the two ESR spectra shown in Figure 1 is very different. Nylon 6 secondary radicals decay to no ESR signal in a few minutes, while the primary radical-picric acid product decays over several hours. The reactive moiety in picric acid is the nitroaromatic structure, as may be seen from the pre-coating results shown in Table 1. Phenol itself, two other aromatics, and an aliphatic nitro-compound are unreactive toward any nylon radical. Only nitrobenzene shows similar interaction to that of picric acid. Neither picric acid, benzene, nor absolute ethanol causes any reaction with secondary nylon radicals. The carbon-centered, aliphatic free radicals assigned to (secondary) nylon spectra (1) are known to abstract hydrogen from a large range of molecules (2). Inertness toward either an acid or an alcohol raises some question as to whether such assignments are correct.

The interception of primary nylon 6 radical by picric acid is relatively efficient. Immediately following fracture, the picric acid radical accounts for 2/3-3/4 of the signal intensity, and the "normal" nylon radical the remainder. This points to

intimate contact of the coating with the nylon fibers. Optical microscopy confirms this. Generally uniform, smooth coating of the individual fibers is noted, with penetration of the yellow picric acid coloring into the fibers. Only a very small fraction of fibers shows an agglomerated coating, perhaps due to excess picric acid which crystallized when the solvent evaporated.

II. Free radical production in energetic materials.

The nylon coating studies described in Part I established that mechano-radicals interact with energetic materials. Our interests have now focussed directly on the free radical activity of the energetic materials proper. This was stimulated by two factors. First, Marinkas, Owens and Vorick, at the Army's Picatinny Arsenal, showed that the free radical signals obtained by shocking energetic materials sub-critically were similar to those produced by UV irradiation (3). This appeared to remove the constraints of mechanical methods of free radical production. Second, ESR examination of a sample of UV-irradiated TATB (sym. triaminotrinitrobenzene) obtained from D. Loughran of Los Alamos Scientific Laboratory showed a large ESR signal from a remarkably stable free radical. TATB's extremely low sensitivity is not altered by the presence of rather large amounts of this free radical irradiation product.

It appeared that the techniques we have developed for examining fast free radical mechano-chemistry in energetic materials could be well utilized in irradiation studies, and so several preliminary investigations were carried out on energetic materials.

A. TATB (sym-triaminotrinitrobenzene).

ESR studies of UV-irradiated TATB showed ready conversion to stable free radicals. An intense green or greenish-black color is associated with the free radical production. Consequently, the UV irradiation is effective in producing only a surface layer of radicals. Exposure of fresh TATB surface results in further radical formation; in this way, we have achieved substantial free radical concentrations. Conversion appears to be limited only by the particle size and may be quantitative in the limit of full bulk exposure.

The TATB radical signal so far observed is structureless: A single, slightly skewed line of half width 5.5 gauss, at $g = 2.0054$. The provocative idea that the signal may originate from trapped electrons (4) is not indicated by the large g -value and the thermal stability of this radical. However, exchange mechanisms may be present which produce "trapping" between molecular sites.

Irradiation of small single crystals of TATB has so far not produced ESR spectra showing anisotropy, as had been hoped. Heating unirradiated TATB to 300°C causes no conversion to free radicals; apparently, free radical formation requires more energy than can be achieved by a thermal process.

The unusual thermal stability of the TATB radical was shown by heating UV-irradiated samples of TATB in the ESR cavity. There is no change in radical intensity or lineshape up to 220°C. During heating to 300°C, the radical decays with a half life of 20 minutes to a new free radical (no asymmetry, yield about 30%) which has a half life of 55 minutes at 300°C. The g -value of the new radical is 2.007, and the half-width is 9.5 gauss.

Solution studies of TATB have also begun. TATB is very sparingly soluble in polar solvents such as N-methylpyrrolidinone and dimethyl sulfoxide (DMSO). Irradiation of such solutions is reported to produce a color change to green (5). We have observed only a color change to orange under UV irradiation. Dr. Carl Heller (NWC/China Lake) obtained results similar to ours using sunlight (6).

Interestingly, we have observed that if irradiated TATB is placed in DMSO, a brownish component is seen to readily dissolve. The filtered solution shows an ESR signal at $g = 2.00$, with half-width 7 gauss.

B. Nitroguanidine (NQ).

NQ pellets (100 mg nominal) pressed to 30 ksi and subjected to sub-critical doses of electron beam irradiation showed stable free radicals (Figure 2) which were apparently trapped in the partially polymerized residue (melamine type plastic). By contrast, NQ irradiated by UV at -196°C was reported to show a free radical signal which decayed quickly upon warming the sample (7). We obtained similar results when we repeated this experiment at -90°C . We were unable to detect a free radical signal in NQ irradiated by UV at room temperature.

C. HMX.

Sub-critical electron beam irradiation of PBX9404 (94% HMX) produced stable free radicals similarly to NQ, but the ESR spectrum of PBX9404 contained a great deal of structure (Figure 3). We have not as yet analyzed this spectrum.

Complementary experiments involving HMX have been carried out under contract by Dr. K. S. DeVries, University of Utah. The samples studied were 10% to 50% by weight HMX in polycaprolactone and polyethylene glycol propellant binders, supplied by Dr. Russell Reed, NWC, China Lake. Free radicals were produced by grinding, by impact, and by gamma irradiation, all at liquid nitrogen temperature. The samples were kept under liquid nitrogen and transferred to the cooled ESR cavity for observation of the free radical spectra as a function of temperature. Special procedures were developed to exclude oxygen from the samples; reactions to form peroxy radicals otherwise occurred rapidly even at the cryogenic temperatures.

The ESR signals appearing in the wings of the spectra (ca 150 gauss) were attributed to HMX on the basis of their rapid disappearance (five-minute half-life) at annealing temperatures as low as -100 to -130°C. These are unusually short half-lives for such low temperatures and indicate radical species of very low stability.

Experiments with HMX-free binders should unequivocally establish the portion of the signal which is due to radicals from the HMX.

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TABLE 1

NYLON 6 COATING EXPERIMENT

I. PRECOATING (INITIAL + SECONDARY RADICALS)

PICRIC ACID - - - - REACTION; NEW FREE
RADICAL STABLE IN AIR

PHENOL - NR (NO REACTION)

BENZENE - NR

ANTHRACENE - NR

2,2 - DINITROPROPANE - NR

NITROBENZENE - REACTION

II. POSTCOATING (SECONDARY RADICALS ONLY)

PICRIC ACID - NR

BENZENE - NR

ETHANOL (ABSOLUTE) - NR

ESR SPECTRA

**NYLON 6 with
PICRIC ACID**

NYLON 6

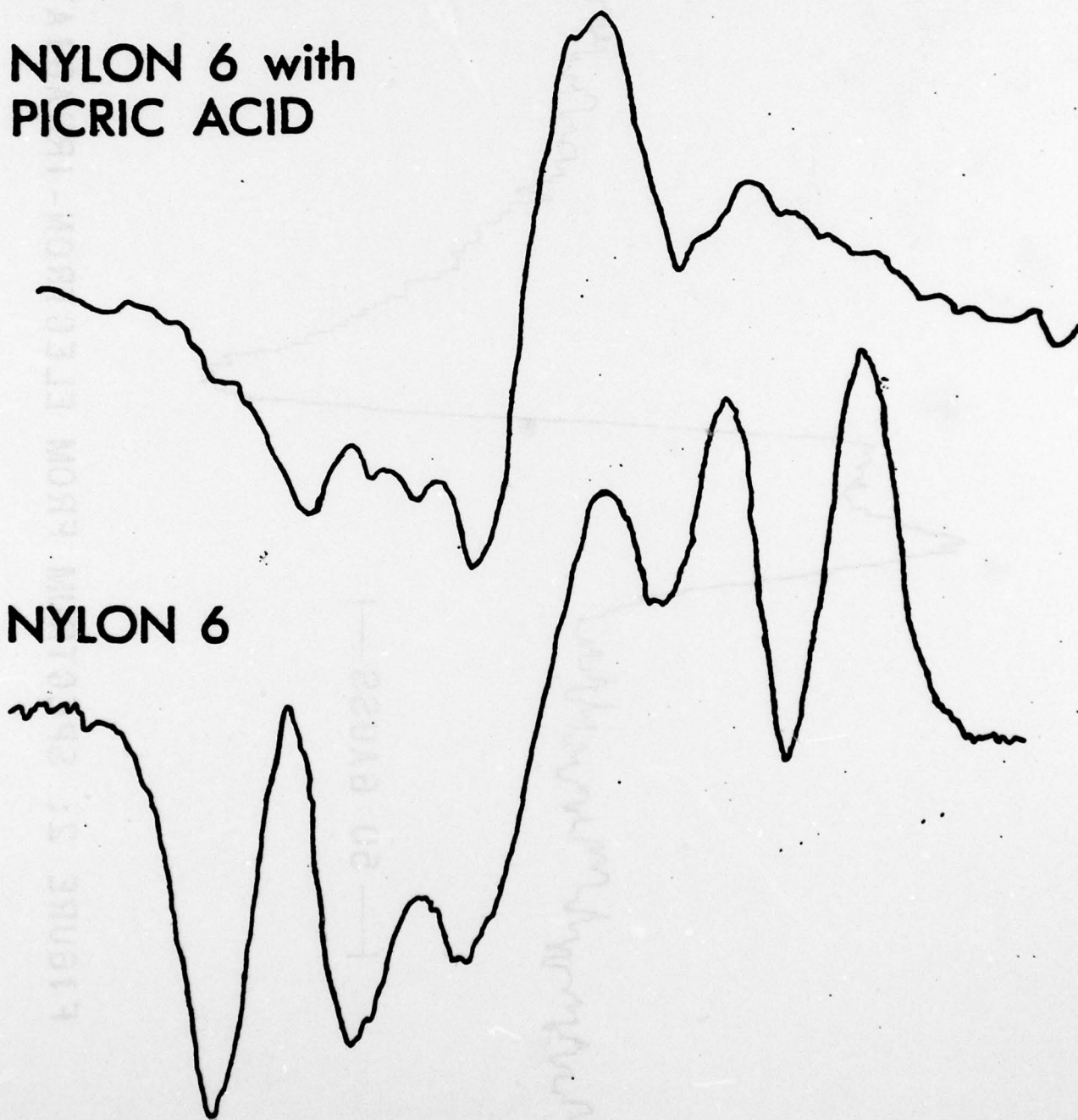


FIGURE 1

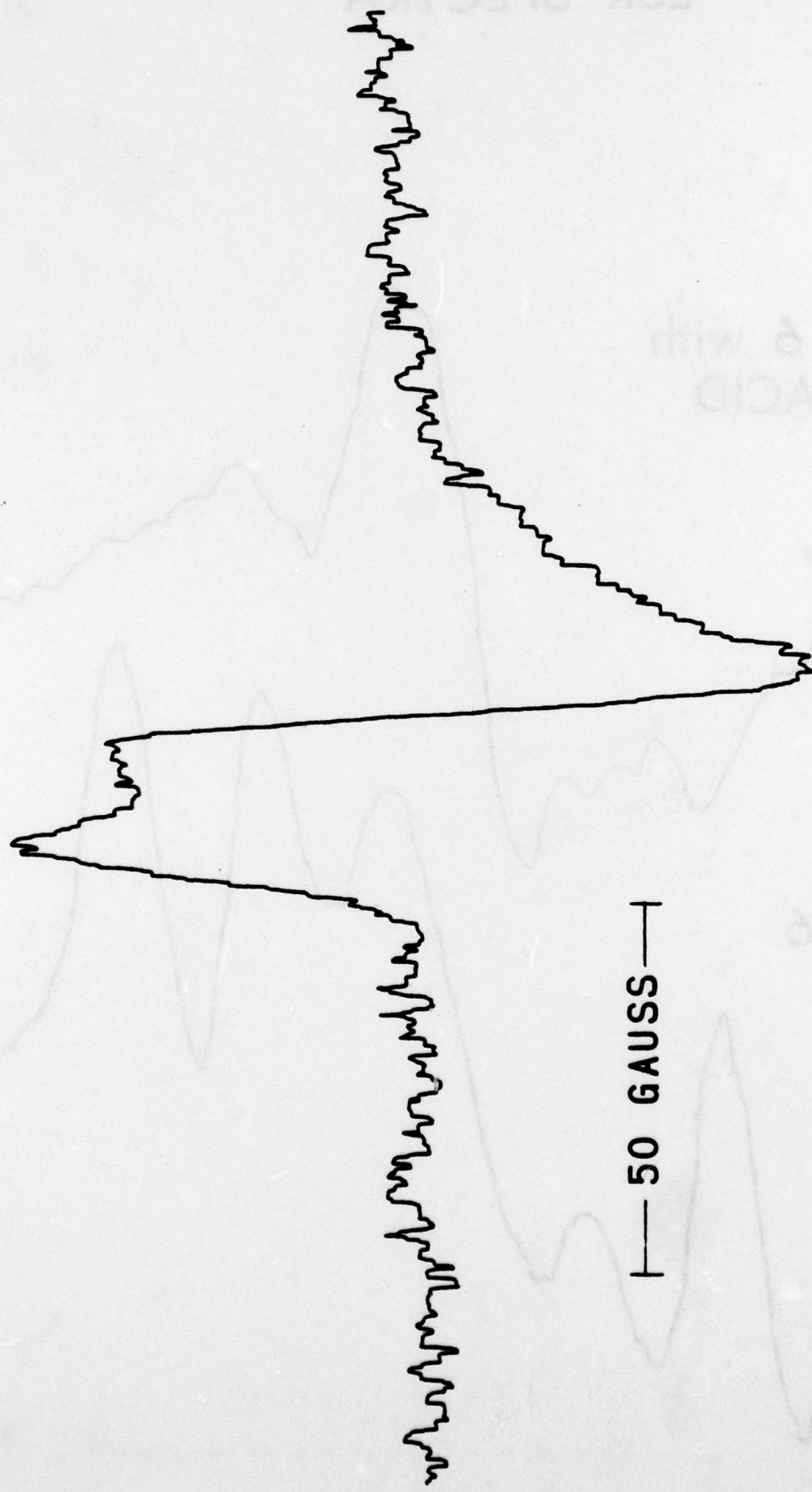


FIGURE 2: SPECTRUM FROM ELECTRON-IRRADIATED NQ

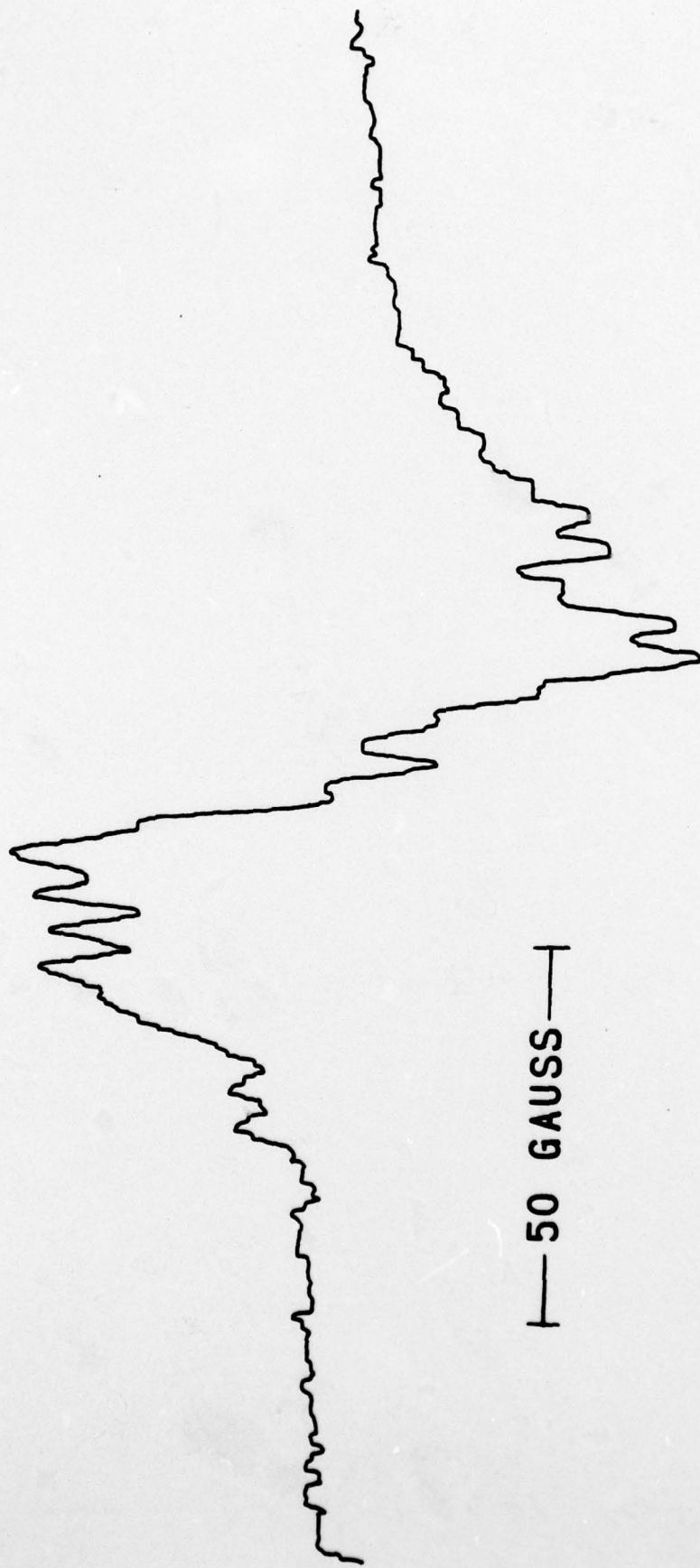


FIGURE 3: SPECTRUM FROM ELECTRON-IRRADIATED 9404

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