# Free radicals in γ-irradiated PETN

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An EPR investigation of γ-irradiated PETN (Pentaerythritol Tetranitrate) was conducted. Low temperature irradiation accumulates at least two different radicals. The more stable radical is the $NO_2$ radical presumably produced by photon cleavage of the $NO_2$ groups and/or by radical reactions in excited states resulting in detached $NO_2$. The spectrum of the more reactive radical is obtained by computer substraction. Decay kinetics are proposed for the $NO_2$ and the unknown highly reactive radical.

## 1. Introduction

Details of molecular rupture in energetic materials are difficult to establish. Molecular bonds can be broken via mechanical stresses, thermal excitation, and by photon irradiation [1, 2]. When the molecular fragments result in unpaired electrons, Electron Spin Resonance (ESR) is a sensitive experimental method by which they might be observed [1, 3]. Since under usual conditions in most materials the unpaired electrons (free radicals) are inherently reactive species the problem is to prevent the free radicals from quickly reacting with each other or impurities and decaying away. Such decay removes direct evidence of their occurrence. It seems well established that the radicals observed are most often not the primary radicals formed by the initial chain scission [4]. At liquid nitrogen temperature many organic free radicals are quite stable and may be "frozen in" and thus may often be generated and accumulated in relatively high concentrations. Radical reactions may be investigated by subsequent warming of the radical filled materials. Instances whereby such reactions lead to a spontaneous increase in free radical concentrations have been reported [5, 6]. Recently, γ-irradiated HMX containing large concentrations of radicals near liquid nitrogen temperature have self-ignited when exposed to (and perhaps triggered by) minor mechanical movement or temperature increase [1].

This laboratory has been interested in the possible role of free radicals in energetic material decomposition. Butyagin [7] has pointed out that the formation of electrically neutral decomposition products, i.e. free radicals or neutral molecular fragments, is favoured over ionic products on simple energy considerations. It has been proposed that radicals once produced may react via chain mechanisms producing further molecular disruption, most likely producing additional free radicals and neutral molecular fragments. It is interesting that Ornellas and McGuire [8], using isotopic labeling, have inferred that almost all of the chemical bonds are broken by a detonation produced inside a calorimetric bomb. As support for this hypothesis they present evidence that the carbon and oxygen isotopes in the final state detonation products, i.e. products like $H_2O$, $CO_2$, CO, $CH_4$, C, are recombined in an isotropically statistical random fashion. Owens and Sharma [9] presented evidence that shock pulses not strong enough to produce detonation in RDX may rupture about 14% of the N—N bonds holding the nitro group to the ring.

Bowden [10] has reasoned that for molecular crystals such as PETN fracture most likely separates molecules of a crystal rather than rupturing the stronger covalent bonds within the molecules. He thus concluded that it is unlikely that a "mechano-chemical" mechanism would apply to

organic explosives. However, Fox and Soria-Ruiz [11] fractured PETN and used a mass spectrometer to analyse the gaseous fragments produced. Their results indicated that the molecule cleaves at the four central C–C bonds producing fragments of the type $CH_2$–$NO_3$ and detectable amounts of $NO_3$–$CH_2$–$C$–$CH_2$–$NO_3$. They concluded that these fragments apparently decay toward CO and NO products.

In HMX, RDX, and PETN the dominant, fairly stable radical, produced by $\gamma$-irradiation is the $NO_2$ radical. Around $0°C$ this radical is reactive with an initial rapid decay. This is followed by a much slower decay so that the $NO_2$ radical can be detected after days at this temperature. $NO_2$ and NO with 17 and 11 outer electrons are paramagnetic. These nitrogen radicals react readily with other radicals often being efficient inhibitors of chain reactions [12]. $NO_2$ is known to absorb ultraviolet light and initiate many photochemical reactions [12]. $NO_2$ radical degradation in HMX, RDX, and PETN materials is apparently not yet understood.

In propellant materials filled with HMX, $\gamma$-irradiation again produces the $NO_2$ radical and another radical presumed to be associated with the polymer structure [1]. Interesting kinetics for the reaction of these radicals will be presented in a subsequent paper. Impact stresses in HMX filled propellant materials produce yet another radical. This is the peroxy radical apparently formed by reaction of the initially produced radicals with oxygen [1]. Oxygen is known to readily react with many primary polymer radicals forming relatively stable peroxide radicals. The primary radical in the binders studied appears to be very unstable and without the inadvertent presence of absorbed oxygen it may have been extremely difficult to present evidence that such low stresses can easily produce free radicals in these systems [1].

Recently, studies of energetic materials using ESCA (Electron Spectroscopic Chemical Analysis) and XPR (X-ray Photoelectron Spectroscopy) have become popular. These methods appear to us to compliment the ESR measurements in that they have some advantages but also some limitations. Measurements are usually performed at room temperature and are limited to regions at or near the surface. Furthermore, a sizeable fraction of atoms must have their chemical neighbours altered. In such *post mortem* methods, very useful in many respects, the details of bond breaking remain obscure.

As noted previously, investigators have expressed interest in the possible role of free radicals in energetic material decomposition [13–15]. Since we have not been successful in correlating the relatively stable $NO_2$ radical concentration in HMX to the increase in impact sensitivity produced by $\gamma$-irradiation, it was speculated that the $NO_2$ radical is not a chain propagating radical in explosive systems [16]. If this is the case other physical changes due to bond rupture must somehow account for the large reported increase in sensitivity of HMX in fallhammer experiments [16]. Dick [17] finds that the time for a detonation wave to overtake an 8.4 GPa shock in PETN is reduced from 1.5 $\mu$sec to 0.94 $\mu$sec for an irradiation of 1 megarad. He reported that a sample aged for 34 days after irradiation was more sensitive than one aged for three days at ambient conditions. This might be viewed as evidence that mere radical concentration is not sufficient to explain the results.

Dickinson *et al.* [18] have observed emission of electrons and positive ions associated with the fracture of a wide range of materials. Dickinson and Jensen [19] have proposed that subsequent reactions of fracture generated radicals may provide the energetics for the observed fracto-emissions.

Fracto-emission from PETN and HMX have been observed by Miles and Dickinson [20, 21]. Both electron and positive ion emission were observed. The results indicate that fracture of PETN breaks intramolecular bonds. The observed continued emission following fracture indicates that freshly fractured surfaces remain chemically reactive for several minutes following fracture. Fracto-emission studies offer very high sensitivity since the single electrons and ions counted during and subsequent to fracture are well above threshold sensitivity of the equipment. The kinetics of fracto-emission and free radical decay have very similar features.

The work reported here emphasizes the search for more reactive radicals in organic explosives than the commonly observed $NO_2$ radical. We report here only the unique results peculiar to PETN.

## 2. Experimental methods

PETN samples were radiated using gamma-rays from a 5050 Curie caesium source. Samples of PETN were sealed in evacuated quartz tubes. The
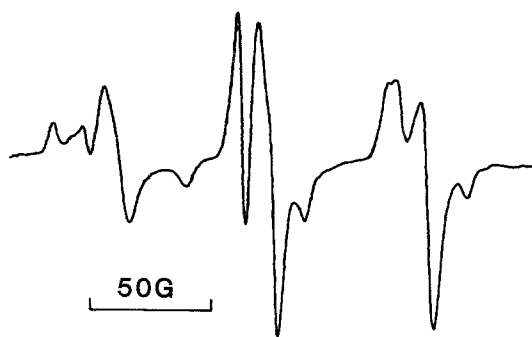
*Figure 1* ESR spectrum of γ-radicals in polycrystalline PETN. Spectrum taken immediately after short term irradiation.

sample tubes were immersed in liquid nitrogen inside a specially constructed irradiation dewar. Samples of PETN were irradiated up to a dose of two megarads. After irradiation, the sample end of the quartz tube was immersed in a small nitrogen dewar so that the protruding portion of the quartz tube could be heated with a torch. This heating completely removed the γ-ray induced "colour centres" with their associated unpaired electrons from the heated end of the quartz. The quartz tube containing the sample was then immersed in a large liquid nitrogen bath and then inverted, allowing the sample to slide down to the colour centre free end of the quartz tube. The quartz tube containing the sample could then be quickly transferred to the pre-cooled low temperature accessory in the microwave cavity of the Varian E-3 ESR spectrometer. Temperature control was achieved using a Varian E-4540 variable temperature controller. First results yielded a radical electron-spin spectra for polycrystalline PETN essentially identical to the commonly observed triplet $NO_2$ radical observed in irradiated HMX and RDX [1, 5]. With experimental care and quickness the presence of a second radical was unambiguously demonstrated. Fig. 1 shows the ESR spectra of polycrystalline PETN measured after only 12 min from the time of the cessation of the γ-irradiation. There is evidence of the superposition in the spectra shown in this figure of at least two radicals. The less stable of these radicals disappears almost completely when the sample temperature is maintained $-120°$ C for only five minutes. Even at liquid nitrogen temperature the less stable radical decays to the limit of detection in several hours. Fig. 2 shows the ESR spectra for the more stable of the radicals which is presumed to be the $NO_2$ radical.



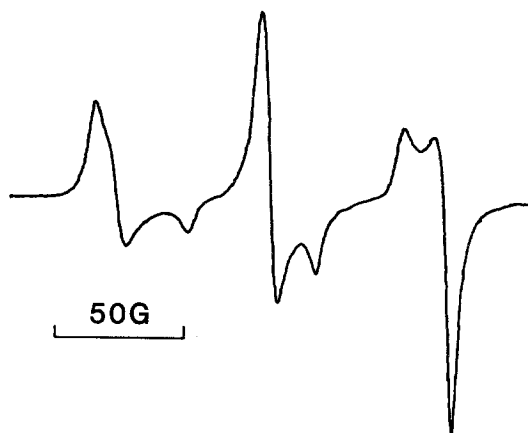*Figure 2* ESR spectrum of γ-radicals in polycrystalline PETN after annealing at $-120°$ C.

The spectra of Fig. 2 was obtained from that in Fig. 1 after an approximately 10 min anneal at $-120°$ C. Fig. 3 is the spectra of the unknown radical obtained by computer extraction from Figs. 1 and 2. Double integration yields the ratio of 0.96 for the ratio of the total spins comparing Fig. 2 to Fig. 1. This demonstrates that there is a one to one conversion of the less stable radical to the presumed $NO_2$ radical. The authors have observed this near 100% efficient conversion of primary to secondary radicals in several polymer systems. Comparing the spins indicated in Fig. 1 with those in Fig. 3 suggests that for this sample there are approximately 2 $NO_2$ radicals for every one of the more reactive (but unknown) radicals. This latter ratio would of course be a function of the sample's radiation and storage history. Presumably some of the $NO_2$ radicals may be formed directly by the radiation while others are most certainly secondary radicals produced by conversion of primary radicals produced by irradiation. These studies clearly indicate that this conversion takes place even at the cryogenic temperatures at which radiation and transportation occurred. One would expect therefore that for radiation with a
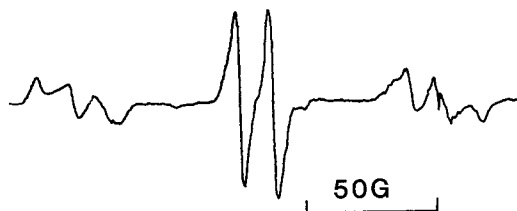


*Figure 3* Computer extraction of relatively unstable radical in PETN. Obtained by subtraction between the spectrum in Figs. 2 and 1.
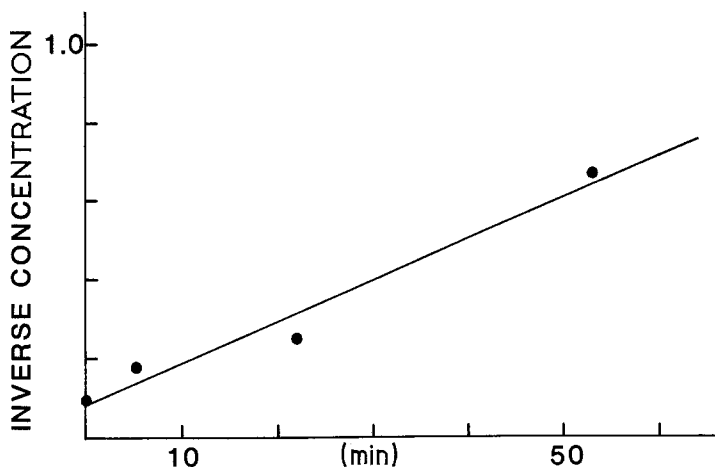
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*Figure 4* Free radical decay curve of the unstable radical, represented in Fig. 3, at −140°C.

very intense source and without short transportation times the ratio of more unstable to stable radicals would be higher. All of the ESR spectra reported here were measured at −150°C.

There is also interest in the stability of free radicals in PETN. Fig. 4 shows the decay of the unknown reactive radical at −140°C. Each measurement in this figure involved decreasing the temperature to −150°C for about four minutes to record the spectra, before rewarming and maintaining at −140°C for the time indicated in Fig. 4. Fig. 5 shows the decay of the $NO_2$ radical at 0°C. Here the quartz sample was simply maintained in an ice water mixture inside a stainless steel dewar between measurement of residual ESR scans. After each period of ice water annealing the sample was quickly transferred to the precooled microwave cavity. Again all these ESR measurements were at −150°C.

## 3. Conclusions

Firm evidence has been obtained, for the existence of an unstable radical in PETN irradiated at liquid nitrogen temperature. So far we have not positively identified this new radical represented by the EPR spectrum shown in Fig. 3. There is a very obvious doublet structure superimposed on the triplet pattern. Mean triplet spacing is roughly 70 G with a central splitting of about 13 G. Our estimate of the average g-value for the central maxima is 2.001. It seems to us that this radical is most likely some combination of nitrogen and hydrogen coupled to the unpaired spin.

While many organic radicals are prone to be quite stable at cryogenic temperatures this unknown radical decays away even at liquid nitrogen temperature. The exact quantitative numbers presented in Fig. 4 may be somewhat suspect since we merely used the extreme left most peak height to
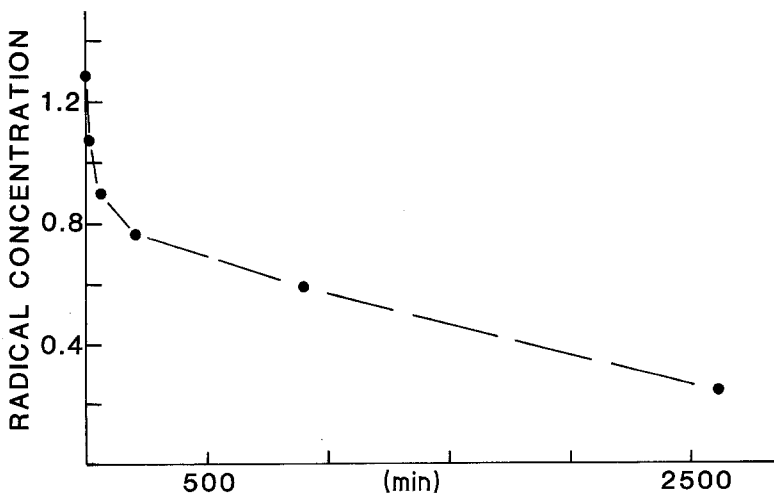


*Figure 5* Free radical decay curve for the $NO_2$ radical at 0°C.

estimate this radical's concentration but the general trends should be as indicated. Analysis of the data of Fig. 4 indicates that it is well approximated by second order decay kinetics. The radicals essentially disappear at this temperature $(-140^\circ C)$ in about one hour. All signs of the radical disappear in about four hours when stored at liquid nitrogen temperature. Several measurements were made to observe this decay. Transfer to a precooled cavity at $-150^\circ C$ was performed for each measurement. The sample would be at (hopefully never warmer than) $-150^\circ C$ for about 5 min per measurement.

The decay of the $NO_2$ radical at $0^\circ C$ did not appear to fit first or second order kinetics. There seemed to be a faster initial decay followed by slower decay. A fast decay followed by a slower decay has often been described by a diffusion controlled reaction [22, 23]. The diffusion controlled reaction valid for a bimolecular reaction $A + B \rightarrow AB$, and for equal initial concentrations of A and B yields a form

$$\frac{C(0)}{C(t)} = 1 + A\ t^{1/2} + Bt.$$

We were unable to fit our rather limited decay data to this form. Detectable concentrations of the $NO_2$ radical were still present after several days at $0^\circ C$.

Double integration of the sample presented in Figs. 1, 2, and 3 indicate that the total spin concentration remains essentially constant as the reactive radical decays away. It is tempting to infer that there is a simple conversion to the $NO_2$ radical. The actual situation may be much more complicated. Neutral nonradical molecular fragments may also be created as the reactive radical disappears. The presence of nonradical fragments is difficult to establish but what can be said with certainty is that for the disappearance of each reactive radical a $NO_2$ radical appears.

The possibility that radiation may produce the $CH_2-NO_3$ radical deserves some comment. However this appears to produce a carbon centered radical and cannot without some additional atomic rearrangements account for the unknown radical observed.

The results from fracto-emission [20, 21] strongly support the notion that mechanical fracture on organic explosives does indeed produce free radicals. The failure to detect free radicals in impacted RDX and HMX is probably due to insufficient concentrations being generated and accumulated because of low production rates and/or fast decay kinetics. This provides additional evidence for the excellent sensitivity of the fracto-emission technique. The authors feel this new technique deserves further exploration.

## Acknowledgement

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