# ESR Study of Free Radicals in the Pyrolysis of Picric Acid

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The free radicals formed in the pyrolysis of picric acid (PA) are observed by the ESR method. The triplet lines with a hyperfine splitting constant of 28~29 gauss can be attributed to the radical, $>C=NO\cdot$. The radicals may be formed by the decomposition of the nitro groups in the *para* positions and the *ortho* positions.

The change of the ESR signal intensity with time below 210℃ is measured in a vacuum. The integrated areas from the curves are proportional to the lifetime of the radicals.

## 1. Introduction

The electron spin resonance (ESR) specra of aromatic nitro compounds heated above their melting points have been observed by Janzen[1], and he also has reported that a hydrogen atom transfer mechanism seemed most feasible for the radical formation in the case of nitrophenols from the result on the effect of structure and temperature in the pyrolysis. He shows that the radicals in nitrophenols such as *p*-nitrophenol and picric acid (PA) have been detected at 140℃ and 130℃ respectively.

When the present author heated pure PA at various temperatures, the radical appeared at 170~180℃. The temperature at which the radicals are formed may differ in the purity and the heating condition of PA. Kast has reported that PA began to decompose slightly, and an insignificant evolution of gases occured when he heated PA at 160℃[2]. Hara et al. have also reported that PA decomposed at 160℃ with evolution of NO₂ on heating, and changed little in its structure up to 260℃[3]. The facts suggest that the radical formation may take place in the decomposition of nitro groups at the temperatures 160~180℃. The author attempted to analyse the hyperfine structure of the ESR spectrum of the radicals, in order to comfirm

whether the radicals are formed by the decomposition of the nitro groups in PA. This paper also discusses on the significance of the change of the signal intensity with time at various temperatures on the basis of the result of the ESR measurement.

## 2. Experimental

### 2.1 Materials.

PA (mp 122~122.5℃) was purified two times by recrystallization in twice distilled water. *o*-Nitrophenol (mp 45.5~46℃) and *m*-nitrophenol (mp 97~97.5℃) were purified two times by recrystallization in ether, respectively, and *p*-nitrophenol (mp 114~115℃) was prepared in toluene in the same way. Ether and toluene were fractionally distilled before use. These mononitrophenols were used in order to investigate the effect of the number of nitro groups on the ESR spectra.

### 2.2 Measurement.

The ESR measurement was carried out using a JEOL PE-1X X-band spectrometer. 100 KHz field modulation and phase sensitive detection at this frequency was used to obtain the first derivative spectra. The temperature of the cavity was controlled with a standard JEOL variable temperature accessory being possible to regulate ambient temperature up to 300℃, and being controlled within ±1℃. PA was placed in the standard quartz tube, and the ESR spectrum was measured in an air and in a vacuum. When

— *313* —

the spectrum was measured in a vacuum, the sample tube was sealed off under a vacuum of about $10^{-5}$ mmHg after permitting to stand for one hour.

### 3. Results and Discussion

#### 3.1 Effect of Temperature on ESR Spectra.

In order to observe the change of the ESR spectrum in an air, the sample was heated by raising the temperature by 10℃, and it was left every 20 minutes. The triplet spectrum with a hyperfine splitting (hfs) constant of 28 gauss and with a peak-to-peak line width ($\varDelta H_{msl}$) of 2 gauss appeared at 180℃ as shown in Fig.1(a). One component of the triplet at the high-field side splitted into a doublet assymetrically. When the temperature was raised higher, the intensity of the triplet increased up to 200~210℃ but disappeared after a few minutes, which was shown in Fig.1 (b). In the temperature region between 220~250℃ the triplet appeared again. This triplet with a hfs constant of 29 gauss and with a $\varDelta H_{msl}$ of 3 gauss is shown in Fig.1(c). The spectrum was not so stable that it changed immediately into a sing-



(a)
180°C

(b)
210°C

28 gauss

(c)
230°C

(d)
260°C

H ⟶

Fig. 1 Change of the ESR spectrum of PA heated in air.

let as shown in Fig.1 (d). The singlet has a $\varDelta H_{msl}$ of 4 gauss. After that, the temperature was raised up to 300℃, the singlet changed no more except its intensity. When the triplet changed to the singlet, the sample was found to be carbonized. In the spectrum in Fig.1(c), the intensities of the triplet are not observed in the ratios approximately 1:1:1. The center line of the triplet apparently increases in its intensity due to overlapping with the triplet and the singlet. Because the spectra in Fig.1(a) and Fig.1(c) may be due to the same type of radicals.

On the other hand, the temperature of the sample was lowered from 180℃ at which the triplet appeared to room temperature step by step. When the sample became solid, the triplet disappeared. When the solid sample was reheated to melt, the triplet appeared again. These behaviors suggest that some decomposition products of PA remain in the sample. The decomposition products may allow to appear the radicals on heating.

When the spectrum of PA was observed in a vacuum in the same manner as the previous experiment, the triplet in Fig.1(a) appeared at 170℃ and changed as Fig.1(b) and (d) in order. The spectrum in Fig.1(c) could not be caught, because PA decomposed more rapidly in a vacuum than in an air.

When the mononitrophenols were studied in the same method as PA in an air, o-nitrophenol gave a spectrum at 290℃, m-nitrophenol at 270℃, and p-nitrophenol at 260℃. Each spectrum was a familiar with that shown in Fig.1(d), and no triplet spectrum could be observed.

#### 3.2 Structure of Radicals.

From the hyperfine splitting of the spectrum and its hfs constant, the structure of the radicals may be cleared. The triplet pattern in Fig.1 arises from coupling to the nitrogen nuclues[1]. In view of the fact, it is most probable that the radicals are formed by a partial decomposition of nitro groups. There have been reported a number of investigations on the radicals, $R_2NO\cdot$ and $RNO\cdot_2$, where R is alip-
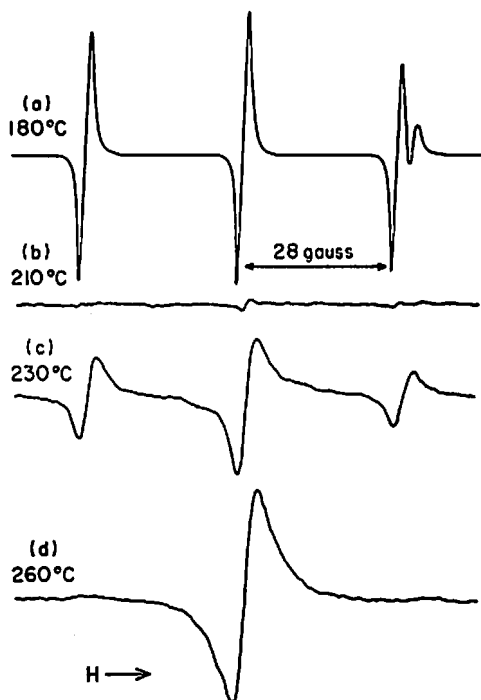
Table 1 Values of the nitrogen hfs constants of the radicals.

| Radical | | hfs constant |
|---|---|---|
| Nitrogen atm . | $\dot{N}$. | 3.7 |
| Nitric oxide | ·N=O ⟷ N-O· | 14.2 |
| Nitrogen dioxide | ·N⟨O⁻ / O· ⟷ N⟨O· / O | 47.1 |
| Nitro anion radical | ·N⟨O⁻ / O⁻ ⟷ =N⟨O⁻ / O⁻ | 1 -16 |
| Nitroxyls | ⊃N-O· ⟷ ⊃N̈-O⁻ | 10-18 |
| Iminoxyls | ⊃C=N-Ö· ⟷ ⊃C=N̈-O⁻ | 28-33 |

hatic or aromatic groups. Table 1 shows the values of the nitrogen hfs constants of the radicals which may be produce in the pyrolysis of PA[5)-14)]. The triplet with a hfs constant 28 ~29 gauss in Fig.1(a) and (c) may be attributed to the radical, >C=NO· being called the iminoxy radical by Thomas[14)], for the value is very close to those of other kinds of iminoxy radicals reported. The radicals may be formed by the partial decomposition of nitro groups in the *para* positions below 210℃, and in the *ortho* positions above 210℃. This view is supported by the facts that the triplet disappears below 210℃ and then appears again above 210℃, and that the nitro groups in *ortho* positions are more stable than those in *para* positions for the reason of internal hydrogen bonding between the nitro group and phenolic group. Indeed, in accordance with the previous result, *p*-nitrophenol began to carbonize at lower temperature than *o*-nitrophenol did.

One component at the high-field of the triplet splitted in addition into a doublet asymmtrically as described in Fig.1(a). It is assumed that the additional line is a partial resolution one of the further hyperfine structure arising from the interaction between the nitrogen nuclues and ring protons. The additional line seems to be most probable to arise from an anisotropic interaction between the nitrogen and ring protons. If the interaction takes place between the nitrogen nuclues and two non-

equivalent ring protons, the each component of the triplet will split into two doublets. In spite of the view, such splitting was not observed unexpectedly. In general, the well resolved spectrum is observed at the state of diluent solutions at low temperature. In this experiment, the less resolved spectrum may be observed, because the sample is in a molten environment where PA molecules get close to interfere each other.

### 3.3 Line Shape Analysis of ESR Spectrum

If the observed line shape agrees with the Gaussian or the Lorentzian line shape, the area from the curve, which is proportional to the concentration of radicals, can be estimated from the equation $S \approx \Delta H^2_{msl} \cdot h$, where h is the peak-to-peak height. In order to analyse the line shape of the spectrum, the center line of the triplet is observed at 180℃. On this analysis the measured line shape is compared directly with the Gaussian or the Lorentzian line shape [15)]. The result is shown in Fig.2. The measured curve came closer to the Gaussian line shape.
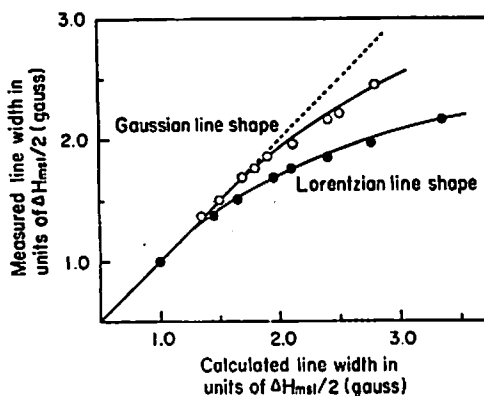


Fig. 2 Line shape analysis of the ESR signal of PA heated at 180℃ in vacuum.

### 3.4 Signal Intensity as a Function of Time.

The triplet observed at 180℃ in a vacuum changed in h but very little in $\Delta H_{msl}$. So the signal intensity was taken as h. The intensity of the center line of the triplet was plotted against time by changing the amount from 0.05 g to 0.3g of PA. The result is shown in Fig.
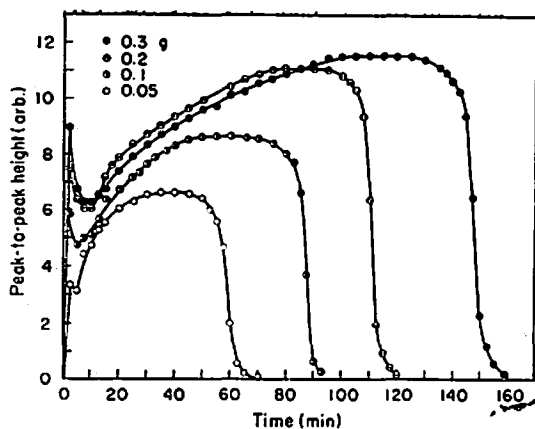
Fig. 3 The time dependence of the ESR
signal intensities of various amo-
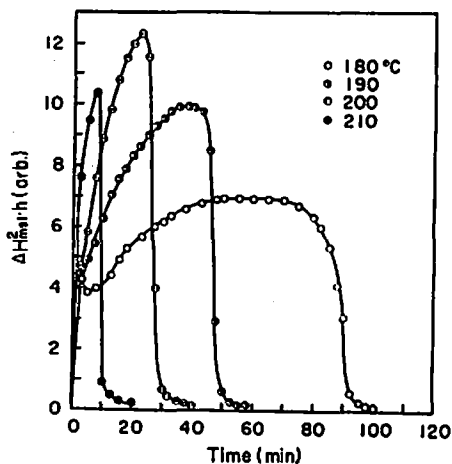unts of PA heated at 180℃ in
vacuum.



Fig. 4 The time dependence of the ESR
signal intensities of 0.1g of PA
which were observed on heating
at various temperatures in va-
cuum.

3. The signal intensity increased to a maxi-
mum after several decades of minutes, which
was held constant in some minutes, and sud-
denly decreased. This pattern did not change
regardless of the amount of PA. Moreover,
the signal intensity was independent of the
amount of PA, but the time of the radical for-
mation became longer as the amount increased.
These phenomena suggest that the mechanisum
of the radical formation is not differ according
to the sample amount, and the radicals are

formed preferentially in a part of the sample in
the tube. It may be reasonable to consider that
the radicals would be produced along the wall
of the sample tube. Next, 0.1g of PA was
heated at temperature 180～210℃, and the trip-
let was observed as a function of time. The
line width changed at temperatures 180～210℃,
since the signal intensity was represented by
$\Delta H^2_{mal} \cdot h$. The signal intensity of the center
line was plotted against time, which are shown
in Fig.4. The result indicates that the higher
the heating temperature rises, the faster the
intensity reaches a maximum.

The change of the signal intensity with time
as shown in Fig.3. and Fig.4 can be explained
from the following equation:

$$\frac{d(\cdot R)}{dt} = V_f - V_d$$

where $\cdot R$ is the concentration of radicals at
time $t$, $V_f$ and $V_d$ are the rate of the radical
formation and the radical decay at time $t$. While
a condition is $V_f > V_d$ in the above equation,
the signal intensity increases with time. When
a condition changes to $V_f < V_d$, the signal in-
tensity begins to decrease with time, and sig-
nal cannot be observed at last. The faster the
rates of the radical formation and decay are,
the more the time required for the concentra-
tion of radicals to be reached a maximum will
shorten. On this report, the experiment is not
sufficient to be discussed the process of radical
formation and decay observing in the pyrolysis.

When 0.1g of PA was heated at 180℃, the
signal intensity being held constant $(V_f = V_d)$
as shown in Fig.3 and Fig.4 was equivalent to
the radical concentration of approximately $10^{15}$
spins/g. The radical concentration was evalua-
ted by comparing the integrated absorption in-
tensity of the triplet with that for DPPH pow-
der. Those integrated absorption intensities
were obtained by a double integration of the
first derivative curves.

The sum of the existing time of radicals in
this experiment may be estimated from the in-
tegrated areas under the curves in Fig.3. If a
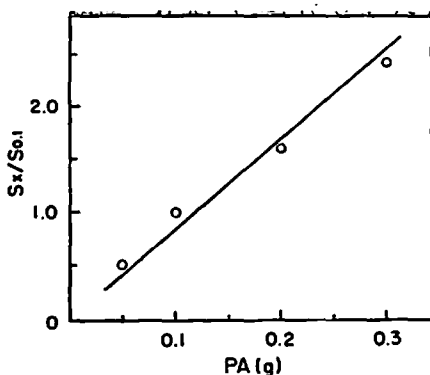radical is formed from a molecule of PA, the

**Fig. 5** Plots of the integrated areas under the curves which were shown in Fig. 3 against the amount of PA.

Sx : Integrated areas obtained by the various amount of PA.

$S_{0.1}$ : Integrated area obtained by 0.1 g of PA.

following equation should be held:

$$\frac{S}{N} \propto \tau$$

where $S$ is the integrated area, $N$ is the amount of PA, and $\tau$ is the mean lifetime of radicals. A plot of the ratios $(S_x/S_{0.1})$ of integrated areas from the curves in Fig. 3 against the amount of PA exhbits a linear relationship as is to be expected from the above equation, and which is shown in Fig. 5. A plot of the ratios $(S_x/S_{210})$ of integrated areas from the curves in Fig. 4 against temperature also gave a good linear relationship. This fact indicates that the lifetime of the radical shortens strightly with raising temperature in the range of $180\sim210°C$. However, it is to be regretted that the above equation could not give the actual lifetime of the radicals.

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# ピクリン酸の熱分解時に生成するラジカルの ESR

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　ピクリン酸の熱分解時に生成するラジカルを ESR 法で調べて次の結論を得た。

　熱分解時にみられるほぼ等強度の3本線（超微細分離定数28～29ガウス）はラジカル >C＝NO・ に起因する。このラジカルは p-位のニトロ基のみならず o-位のニトロ基からも 生成すると思われる。

　シグナル強度の変化を時間に対してプロットして得た曲線と x 軸で囲まれる面積は，ラジカルの平均寿命に比例した量である。

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