Radiation Induced Free Radicals in Alanine and Some Related Amino Acids

Electron Spin Resonance Studies *

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Free radicals induced by ionizing radiation in polycrystalline samples of α-alanine and some related amino acids have been studied by electron spin resonance techniques. The results show that the observed spectra very often represent the composite pattern of more than one radical. Qualitative changes occur in the electron spin resonance spectra, demonstrating that secondary processes take place at a fairly slow rate in the solid state.

The number of induced radicals has been measured as a function of the radiation dose as well as of the time after the end of the exposure. The dose effect curves are straight lines up to a certain dose level and then flatten out. This occurs before any saturation effects are to be expected. Time studies demonstrate the surprisingly high stability of radicals induced and trapped within solid amino acids.

For the amino acids studied, 5–50 electron volts were found necessary to induce one primary radical with lifetime long enough to be observed. These low values seem to imply that the radicals originate not only from ionizations, but also from excitation processes which are subsequently followed by rupture of chemical bonds. Conceivably the radical fragments induced may take part in reactions with intact neighbour molecules, a circumstance which may explain the observed qualitative changes in the resonance patterns.

Radiation induced free radicals trapped in the solid state or in frozen solutions can be studied by electron spin resonance techniques (ESR)\textsuperscript{1–5}. Since the work of Combrisson and Uebersfeld in 1954\textsuperscript{11}, unpaired spins in solid amino acids have been studied by a number of investigators\textsuperscript{6–10}. Thus, Shields and Gordy\textsuperscript{6} have presented qualitative resonance spectra for different amino acids which have been exposed to high X-ray doses, but no quantitative

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results were given. Box and Freund 7 have measured radiation yields for some amino acids. Usually G-values (number of unpaired spins produced per 100 eV of absorbed energy) less than 1 were found. These results seem to be in agreement with those of Randolph and Parrish 8, but differ from the result of Zimmer et al. 9 on glycine. In a recent work Randolph and Parrish 10 have also studied the stability of the induced radicals. They found a very slow decay of spins in a-alanine and glutamic acid during the first 6 months.

In a previous study of thiols and disulphides 12-14 we found that the qualitative and quantitative ESR measurements are influenced by parameters such as the radiation dose, the temperature, the oxygen pressure and the time elapsed between the end of the exposure and the measurements. The results indicated that secondary processes take place at a fairly slow rate in the solid state. These findings are somewhat in conflict with the above mentioned works, and the purpose with the present paper is therefore mainly to extend our work on sulphur compounds to ordinary amino acids. a-Alanine and some related amino acids have been chosen for this purpose. Special attention has been given to the above mentioned parameters. Extensive time studies have been made in order to see if secondary processes take place in these substances as well.

The results show that radicals are induced in these amino acids with surprisingly high yields, a finding which seems to be of considerable interest with regard to the mechanism of radical production.

MATERIALS AND METHODS

The spectrometer. The spectrometer which is described in a previous paper by Henriksen and Fihl 14 operates at a frequency of 9200 Mc/sec. The magnetic field is modulated at a frequency of 110 kc/sec. In the present experiment the microwave frequency is measured with a wavemeter with an accuracy of about 0.1 %, and the magnetic field is measured with a proton resonance field meter. The sweep rate of the magnetic field is 19 gauss/min. The microwave power was small and no saturation effects were observed.

The substances. DL-Alanine, DL-serine, L-cysteine, L-glutamic acid, DL-glutamic acid monohydrate, L-glutamic acid monohydrochloride, L-phenylalanine, L-histidine, L-tryptophane, were purchased from Nutritional Biochemical Corporation. The β-alanine was purchased from Hoffmann-La Roche, and L-aspartic acid from Sigma Chemical Co. The compounds were all of the highest analytical grade. The samples were prepared by grinding the amino acids in a mortar, and each sample consisted of about 10-40 mg dry powder.

The samples were evacuated by a high vacuum diffusion pump and sealed off at a vacuum of 10^-4-10^-5 mm Hg.

Irradiation conditions. A 220 kV Siemens X-ray tube externally filtered by 0.7 mm glass was used. The dose rate was 7700 r/min. The total doses varied between 1 × 10^4 r and 6 × 10^5 r. In most cases the dose was about 1.5 × 10^5 r with an exposure time of 20 min. The doses were measured with an ionization chamber.

The samples were irradiated and measured at room temperature. The first spectrum was usually recorded 10 min after the end of the exposure. Some of the samples were heat treated at controlled temperatures between the exposure and the measurements.

Quantitative procedures. It is generally assumed that the number of radicals are proportional to the area of the absorption curves 1. Since this spectrometer gives the first derivative of the actual spectra, the desired area was obtained by double integration which was performed graphically. In order to obtain the absolute number of free radicals per gram of irradiated compound, the spectra were compared with those of reference samples measured under the same conditions.

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Fig. 1. The upper curve is the spectrum of α-alanine observed 10 min after irradiation, and the 3 lower spectra represent β-alanine observed at different times after the exposure. All spectra in this paper represent the first derivative of the actual absorption curves. The arrows indicate the position of the resonance of DPPH ($g = 2.0036$). The spectra may only be compared qualitatively since different gains were used. The samples were irradiated and stored in vacuum, at room temperature (20°C).

The free radical 1,1-diphenyl-2-picryl-hydrazyl (DPPH) is frequently used as a reference system. When DPPH is crystallized from CS$_2$ both the line shape and the measured area vary with the oxygen pressure. Correct areas are observed when the samples are measured in high vacuum. This oxygen effect is much smaller when the compound is crystallized from benzene or chloroform, but the addition complex now obtained must be chemically analysed. Because of the above mentioned effects we found it inconvenient to use DPPH, and anthracite carbon powder was used in this work. This secondary standard was calibrated against DPPH which was recrystallized from CS$_2$ and measured in high vacuum. The absolute number of spins thus obtained may be off by as much as about 50%.

The energy absorbed by the compound in question was calculated on the assumption that the radiation is absorbed predominantly by Compton scattering.

RESULTS

Qualitative measurements. α- and β-Alanine, when exposed to X-rays, give resonance patterns which are shown in Fig. 1.

\[
\begin{align*}
\text{H} - \text{CH}_2 - \text{CH} - \text{COOH} & \quad \text{H} - \text{CH} - \text{CH}_2 - \text{COOH} \\
\downarrow \text{NH}_2 & \quad \downarrow \text{NH}_2 \\
(\text{I}) & \quad (\text{II})
\end{align*}
\]

Fig. 2. The qualitative spectra of serine and cysteine. The lower serine pattern is observed after heat treatment at 105°C for 16 h. Otherwise conditions as in Fig. 1.

α-Alanine (I), shows a nearly symmetrical 5-line spectrum with an unresolved pattern superimposed. This resonance spectrum which is nearly the same as that observed by Gordy et al.\(^2,6\) was found to be independent of the radiation dose and the time after the end of the exposure. Also, it was unchanged upon heat treatment for several hours at about 110°C. These findings suggest that only one single radical is induced in α-alanine. From work with single crystals Miyagava and Gordy\(^8\) presume the radical to be CH₃—CHR where the unpaired electron interacts with 4 protons, and R is a group which has no detectable coupling.

The resonance pattern of β-alanine (II), on the other hand, is not stable and shows qualitative changes with time (Fig. 1). The initial pattern seems to be more resolved than previously observed by Shields and Gordy\(^6\), and by Randolph and Parrish\(^8\). The central peak with a g-value of 2.0056 increases gradually during the first days, reaches a maximum and then decays slowly and finally becomes smeared out.

It seems to be quite clear that the position of the amino group in alanine modifies the resonance pattern, and in order to get more information about the influence of different chemical groups a number of derivatives of α-alanine were studied. Thus we have studied serine were OH is substituted for one of the methyl protons; (R = OH), cysteine (R = SH),

\[
\begin{align*}
R - CH_3 - CH - COOH \\
\text{NH}_2 \\
(\text{III})
\end{align*}
\]

aspartic acid \((R = \text{COOH})\), different types of glutamic acid \((R = \text{CH}_2\text{COOH})\) and a few amino acids with aromatic rings like phenylalanine, histidine, and tryptophane.

In Fig. 2 the spectra of cysteine and serine are compared. The cysteine spectrum which remains unchanged with time is displaced to a lower magnetic field strength than ordinary hydrocarbon radicals. This increase in \(g\)-value \((g = 2.025\) for the central peak) is consistently found for thiols\(^{13}\) and other sulphur compounds\(^{19,20}\), and the spectrum most likely represents one single radical where the unpaired electron is localized on the sulphur atom as proposed by Gordy and Shields\(^{21}\). When the sulphur atom is replaced by oxygen, a completely new resonance pattern is observed. Thus Fig. 2 shows that DL-serine gives a pattern which initially consists of at least 10 lines, and is about 125 gauss wide. This resonance is quite unstable and after few hours at room temperature qualitative changes are observed. Heat treatment for about 16 h at 105°C completely changes the resonance, and this spectrum does not show further changes. The spectrum, which is now about 140 gauss wide, resembles that found by Shields and Gordy\(^{6}\) for L-serine. The \(g\)-value for the center of the resonance is close to that of DPPH \((g = 2.0036)\). The reason for the great difference between serine and cysteine is not immediately obvious. Whereas the unpaired electron in cysteine seems to be localized on the sulphur atom, no evidence is found from the serine spectra that the unpaired electron is localized on the oxygen atom in this compound.

In Fig. 3 the spectra of aspartic acid and of different types of glutamic acid are shown. The resonance pattern of aspartic acid shows only moderate changes with time, and even heat treatment at 105°C for several hours intro-

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**Fig. 3.** The qualitative resonance patterns of aspartic acid, glutamic acid, and glutamic acid hydrochloride. Otherwise conditions as in Fig. 1.

**Fig. 4.** The qualitative spectra of glutamic acid observed under different conditions. All samples were irradiated at room temperature.

duces only minor changes in the spectrum. The initial spectrum which is about 140 gauss wide consists of 13 unresolved peaks, but after 20 h at 105°C only 10 peaks are observable.

For glutamic acid, which contains one CH₂ group more than aspartic acid, we have studied glutamic acid monohydrate and glutamic acid hydrochloride as well as free glutamic acid. Approximately the same qualitative resonance pattern was found for glutamic acid and glutamic acid · H₂O, whereas a different spectrum was found for glutamic acid · HCl (Fig. 3). The resonance pattern of glutamic acid · HCl was found to be very stable. Thus, after heat treatment at 105°C for 2 days the spectrum remained unchanged. On the other hand, the radicals induced in glutamic acid · H₂O decay rapidly and no spectrum was detectable after 60 min at 105°C. This rapid decay possibly means that the added water acts as bridges for recombination processes.

The initial pattern of free glutamic acid is about 130 gauss wide and shows 7 unresolved hyperfine lines. This resonance is relatively stable, but upon prolonged storage at room temperature the resonance becomes more resolved, and after 7 months the 7-lined spectrum is changed into at least 12 lines (Fig. 4). The qualitative changes which take place very slowly at room temperature, proceed more rapidly but in much the same way at elevated temperatures. In Fig. 4 is shown that the same qualitative changes which are obtained after 7 months at room temperature are reached in the course of 100 min at 105°C. Further heat treatment gives a final spectrum of 13 lines, and it is interesting to notice that this spectrum of glutamic acid shows many similarities to that of aspartic acid (Fig. 3).

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![Fig. 5. The qualitative spectra of histidine observed after different treatments. Otherwise conditions as in Fig. 1.](image1)

![Fig. 6. The qualitative resonance pattern of phenylalanine and tryptophane. The dose for tryptophane was 9 × 10⁶ r.](image2)

Amino acids with aromatic rings have also been examined (Figs. 5 and 6). Both phenylalanine and histidine show a much more resolved hyperfine structure than that observed by Shields and Gordy. The initial resonance pattern of histidine is about 155 gauss wide, a little unsymmetrical, and about 16 hyperfine lines are observable. Fig. 5 shows the spectra of histidine after heat treatment. The resonance becomes symmetrical and with a $g$-value like that of DPPH for the central peak. After 18 h at 105°C only 9 peaks are observable. The initial pattern of histidine shows many similarities with aspartic acid and glutamic acid after heat treatment.

**Table 1. Summary of qualitative data.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>R in formula III</th>
<th>Total with in gauss</th>
<th>Number of peaks initially observed</th>
<th>Qualitative changes with time at 20°C</th>
<th>Qualitative changes with time at 105°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-Alanine</td>
<td>--</td>
<td>95</td>
<td>10 unresolved</td>
<td>small and slow</td>
<td>small</td>
</tr>
<tr>
<td>DL-$\alpha$-Alanine</td>
<td>$-\text{H}$</td>
<td>145</td>
<td>5</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>L-Aspartic acid</td>
<td>$-\text{COOH}$</td>
<td>140 ($\downarrow$) b) 125</td>
<td>13 unresolved</td>
<td>very small</td>
<td>small, 10 peaks after 20 h</td>
</tr>
<tr>
<td>L-Glutamic acid</td>
<td>$-\text{CH}_2-\text{COOH}$</td>
<td>130</td>
<td>7</td>
<td>large, but very slow (months)</td>
<td>large, 13 peaks after 41 h</td>
</tr>
<tr>
<td>DL-Glutamic acid, monohydrate</td>
<td>$-\text{CH}_2-\text{COOH} \cdot \text{H}_2\text{O}$</td>
<td>125</td>
<td>7</td>
<td>small during the first 14 days</td>
<td>no resonance after 1 h</td>
</tr>
<tr>
<td>L-Glutamic acid, monohydrochloride</td>
<td>$-\text{CH}_2-\text{COOH} \cdot \text{HCl}$</td>
<td>140</td>
<td>6</td>
<td>none (3 months)</td>
<td>small during the first 41 h</td>
</tr>
<tr>
<td>DL-Serine</td>
<td>$-\text{OH}$</td>
<td>125 ($\downarrow$) b) 140</td>
<td>$\geq$10 unresolved</td>
<td>large, 12 peaks after 3 hours</td>
<td>very large</td>
</tr>
<tr>
<td>L-Cysteine</td>
<td>$-\text{SH}$</td>
<td>140</td>
<td>3</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>L-Phenylalanine</td>
<td>$\text{C}_6\text{H}_5$</td>
<td>120 ($\downarrow$) 90</td>
<td>$\geq$7 unresolved</td>
<td>small</td>
<td>the hyperfine structure is smeared out after 1 h</td>
</tr>
<tr>
<td>L-Histidine</td>
<td>imidazolyl</td>
<td>155 ($\downarrow$) b) 145</td>
<td>16</td>
<td>none (3 days)</td>
<td>great but slow, 9 peaks after 18 h</td>
</tr>
<tr>
<td>L-Tryptophane</td>
<td>indolyl</td>
<td>120</td>
<td>probably 10 unresolved ($\text{smeared out}$)</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

a) The error in these values is about $\pm$ 10%.
b) The upper figure represents the initial value. The arrow and the lower figure mean that the total width of the spectrum is changed after heat treatment.

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The spectrum of phenylalanine is about 120 gauss wide and 7 hyperfine lines are observable (Fig. 6). This resonance shows many similarities with the spectrum of \( \beta \)-alanine. Upon heat treatment the hyperfine structure is smeared out and the final spectrum is only 90 gauss wide.

Tryptophane gives a very faint resonance even upon prolonged irradiation (Fig. 6). No definite resonance structure can be ascribed to this compound. Both the qualitative and quantitative results show that the radicals are not so easily stabilized in aromatic compounds. The qualitative data here presented are summarized in Table 1.

**Quantitative measurements.** The total number of radiation induced free radicals was measured as a function of the radiation dose (dose-effect curve). In Fig. 7 dose-effect curves are given for the three types of glutamic acid in the dose range up to \( 2 \times 10^5 \) r. The exposure time was 25 min throughout and all spectra were recorded 10 min after exposure. The dose-effect curves are straight lines in the relatively low dose range, a result which agrees with that found for glycine by Zimmer et al.\(^9\). However, when exposed to doses in the mega-röntgen range, it was found that the dose-effect curves flatten out as exemplified for \( \alpha \)- and \( \beta \)-alanine in Fig. 8. This flattening out which we have previously found for a number of sulphur compounds\(^{12-13}\), is difficult to explain. Saturation can hardly account for this effect since it can be calculated that less than 1 out of 1,000 molecules is hit at the dose of \( 1 \times 10^8 \) r. In experiments with doses in the mega-röntgen range, the exposure time varied and one possible explanation for the observed flattening out of the dose-effect curves is therefore that decay processes may occur during exposure.

Extensive studies were made in order to obtain information on the stability of the induced radicals. The total number of observable spins was plotted against the time elapsed after the end of the exposure. The results in Fig. 9 demonstrate the surprisingly high stability of radicals induced in α- and β-alanine. After a slight initial increase in the observable number of free spins, the decay may be described by a straight line in this semilogaritmic plot. In a previous study of sulphur compounds we found that the decay of the total number of spins \(N\) was best described by the formula \(N = a \ln t + b\), where \(a\) and \(b\) are constants. Interestingly, this formula may also be used for amino acids as shown in Figs. 9 and 10. Even decay at elevated temperatures may be described in this way as shown for glutamic acid in Fig. 11. The results for the three types of glutamic acid (Fig. 7 and Table 2) show that three times more radicals are induced in glutamic acid \(\cdot\) HCl than in the two other types of glutamic acid. The data in Figs. 10 and 11 also demonstrate that these radicals are more stable than those induced in free glutamic acid and glutamic acid monohydrate.

The results presented in Fig. 9 clearly demonstrate that the above mentioned flattening out of the dose-effect curves (Fig. 8) cannot be explained by a simple decay process during the exposure. This flattening out may therefore be the result of other processes during irradiation. The possibility should be considered that during exposure the new radicals formed may combine with radicals already formed, and that this process competes with the trapping process. A similar explanation has been proposed by Atherton et al. for the copolymerization of methyl methacrylate by UV irradiation.

The quantitative data from our experiments are summarized in Table 2. In this table the observed yields for radical production are given. Since different parameters influence the ESR measurements, the yields are values extrapolated to the conditions of zero dose, room temperature (20°C), high vacuum \((10^{-4} - 10^{-5} \text{ mm Hg})\), and measurements obtained 10 min after the end of the exposure. Presented in Table 2 are the inverse values of the yield, i.e. electron volts per radical.

![Diagram 1](image1)

*Fig. 9.* The decay of radiation induced radicals in α- and β-alanine at 20°C. O = α-alanine and x = β-alanine. The data are given in per cent of that observed 10 min after irradiation.

![Diagram 2](image2)

*Fig. 10.* The decay of radiation induced radicals in the 3 types of glutamic acid at 20°C. Δ = glutamic acid hydrochloride, O = glutamic acid, and x = glutamic acid monohydrate. The data are given in per cent of that observed 10 min after irradiation.

Fig. 11. The decay of radicals in the 3 types of glutamic acid after heat treatment for varying periods of time at 115°C. The number before heat treatment was set equal to 100 in all 3 cases. The first measurement was made after heat treatment for 10 min. ∆ = glutamic acid hydrochloride, ○ = glutamic acid, and × = glutamic acid monohydrate.

Table 2. Summary of quantitative data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R in formula III</th>
<th>Inverse yields in a) eV/rad.</th>
<th>Decay (in %) after storage for 1 h at 20°C</th>
<th>Decay (in %) after storage for 1 day at 20°C</th>
<th>Decay (in %) after storage for 1 h at 105°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Alanine</td>
<td>-</td>
<td>25</td>
<td>1</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>DL-a-Alanine</td>
<td>H</td>
<td>13</td>
<td>-3 c)</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>L-Aspartic acid</td>
<td>-COOH</td>
<td>17</td>
<td>3</td>
<td>17</td>
<td>22</td>
</tr>
<tr>
<td>L-Glutamic acid</td>
<td>CH₃-COOH</td>
<td>15</td>
<td>8</td>
<td>12</td>
<td>- d)</td>
</tr>
<tr>
<td>DL-Glutamic acid, mono-hydrate</td>
<td>CH₃-COOH • H₂O</td>
<td>15</td>
<td>10</td>
<td>18</td>
<td>- d)</td>
</tr>
<tr>
<td>L-Glutamic acid, mono-hydrochloride</td>
<td>CH₃-COOH • HCl</td>
<td>5</td>
<td>7</td>
<td>11</td>
<td>- d)</td>
</tr>
<tr>
<td>DL-Serine</td>
<td>OH</td>
<td>14</td>
<td>-4 c)</td>
<td>19</td>
<td>23</td>
</tr>
<tr>
<td>L-Cysteine</td>
<td>SH</td>
<td>34</td>
<td>-2 c)</td>
<td>2</td>
<td>&gt;20</td>
</tr>
<tr>
<td>L-Phenylalanine</td>
<td>C₆H₅</td>
<td>36</td>
<td>2</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>L-Histidine</td>
<td>imidazolyl</td>
<td>52</td>
<td>-8 c)</td>
<td>-1</td>
<td>15</td>
</tr>
<tr>
<td>L-Tryptophane</td>
<td>indolyl</td>
<td>265 b)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a) The error in these values may be as much as 50%.
b) The value observed at 9 × 10⁻⁴ r.
c) The total number of observable ESR centers for these compounds increased slightly during the first minutes after irradiation.
d) See Fig. 11.
DISCUSSION

The results here presented clearly demonstrate that qualitative changes with time occur in the ESR spectra of irradiated amino acids. Such qualitative changes could be explained if several primary radicals with different rates of decay were induced. The results for serine, glutamic acid and histidine also demonstrate that the initial spectrum represents the composite pattern of more than one radical. However, when the quantitative results are compared with the qualitative changes in the ESR spectra, it seems that other processes than simple decay take place. In a previous work on glutathione, we found that by such secondary processes the unpaired electron spins may even migrate to one specific group, the sulphur atom of the cysteine residue. However, the nature of these secondary processes is at the moment obscure. The results here presented demonstrate that these processes can be speeded up by heat treatment.

In Table 2 the number of electron volts needed to induce one primary radical is given. The values, ranging from 5 to 50 eV per radical, differ greatly from the results of Box and Freund, and Randolph and Parrish. The values in this work refer to zero dose. When the flattening out of the dose-effect curves is considered, these differences in yield may probably be explained.

The high yields (low values in Table 2) observed may be of interest with regard to the mechanism for the radical production. Up to now it has usually been assumed that the radicals observed are formed from ionization processes and that the observed spins represent positive holes. The negative ions formed from the trapped electrons are assumed to give too broad spectra to be observed.

Very little is known about the primary radiation processes in the solid state. Thus, the energy necessary to induce one ion pair \( W \) is measured only for some semiconductors like Ge and Si, for a few silver halide crystals and for diamond. Surprisingly low values, ranging from 3 eV to 10 eV have been reported. No such data are reported for solid organic compounds. In hydrocarbon gases \( W \) has been found to be about 26 eV. In the gaseous state the ratio \( W/I \) is usually about 2 (\( I \) is the ionization potential). It seems therefore reasonable that the ratio \( W/E \) for solids (\( E \) is the minimum energy to liberate an electron in a solid) will be about 2.

In view of these facts no conclusive statement can be given to the theory that the ESR spectra represent positive holes. However, the radiation yields here presented seem to indicate that also other processes with the formation of radicals may take place. One possible mechanism is that some of the ionized molecules which are in an excited state may undergo a homolytic dissociation and thus give molecular fragments with unpaired spins. In a previous paper we have also proposed the possibility that some of the primary excitation processes are subsequently followed by rupture of chemical bonds with the formation of fragment radicals. Magee and Funabashi have proposed a similar dissociation of excited molecules as one possible mechanism for radical production.

Some of the radical fragments produced by rupture of chemical bonds may have enough kinetic energy to escape an immediate recombination. These
radicals may then be stabilized within a cage of intact neighbouring molecules. It is likely that the radical fragments take part in secondary reactions inside the cage. These reactions are assumed to be rapid and temperature independent. Also reactions outside the cage may occur, but since the radicals now must escape from the cage, these processes are assumed to be slower and influenced by temperature. The results in this work are consistent with such a mechanism.

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REFERENCES


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