Production of Free Radicals in Organic Solids by Thermal

Hydrogen Atoms*

HARALD JENSEN [a,b] and THORMOD HENRIKSEN [a]

*Norsk Hydro's Institute for Cancer Research, The Norwegian Radium Hospital,
Montebello, Norway*

Several amino acids and nucleic acid bases have been exposed, in the solid state, to the products in a hydrogen gas discharge system. These discharge products include thermal hydrogen atoms as well as high-frequency UV light. It was found that the vacuum UV light produced radicals similar to those induced by ionizing radiation in most substances. The UV light was reduced by introducing bends in the discharge system. The exposed substances can be divided into three groups. In the first group, which includes substances such as glycine, alanine, and glycyl-glycine, the radicals were formed by the UV light. In the second group, containing leucine, penicill-amine, and malonic acid, both the UV light and the thermal hydrogen atoms contributed to the radical formation. Finally, in the third group, containing thymine and uracil, the free radicals were formed by the thermal hydrogen atoms. Thermal hydrogen atoms produced radicals either by abstracting a hydrogen atom from a saturated molecule or by adding a hydrogen atom to an unsaturated carbon atom. Since the thermal hydrogen atoms have a limited range in the exposed crystallites, the radicals are formed and trapped in a surface layer only. Calculations based on dipolar broadening indicate a thickness of approximately 0.2 to 0.3 μ for this surface layer. This distribution of radicals makes them readily accessible to diffusible gases and a pronounced oxygen effect was observed.

The damage observed in a biological system exposed to ionizing radiation is usually ascribed to certain reactive primary species such as H atoms, OH radicals, and electrons. Attempts have been made in recent years, especially in pulse radiolysis experiments, to study the effect of the different primary species separately. The effect of hydrogen atoms has also been elucidated in experiments where thermal hydrogen atoms from a hydrogen gas discharge system have been used.[1–13] Similar experiments have also been carried out

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with OH radicals formed by dissociation of water vapor and H_2O_2 in an electric discharge.[4,14]

During the last few years various groups have used electron spin resonance (ESR) spectroscopy to study radical formation in organic solids exposed to thermal hydrogen atoms. Such experiments were initiated by Ingalls and Wall [5-7] who observed free radicals in fluffs of polymers which were placed downstream to an electrodeless discharge in a hydrogen gas flow system. Cole and Heller [8,9,12] have observed free radicals in malonic acid and some of its derivatives as well as in thymine and DNA (deoxyribonucleic acid) after exposure to the products in a hydrogen gas discharge. They concluded that thermal hydrogen atoms produce radicals either by abstracting a hydrogen atom from a C—H bond in a saturated molecule or by addition of a hydrogen atom to an unsaturated carbon in an olefinic type of molecule.

Herak and Gordy [10,11] have studied the free radicals produced by the products in a hydrogen gas discharge system in several pyrimidine and purine derivatives. Finally, Snipes and Schmidt [13] used the ESR technique to study the radicals induced in a number of amino acids. They observed a difference in the oxygen effect between the radicals produced by γ-rays and those formed in a hydrogen gas discharge system which they ascribed to differences in the distribution of radicals within the crystallites.

In some preliminary experiments carried out in this laboratory organic solids were exposed downstream in a right-angle bend tube to the products from a hydrogen gas discharge. It was found that the high-frequency UV light produced by the discharge seriously influenced the radical formation. In the present work efforts have therefore been made to carry out experiments where it is possible to differentiate between the products in the hydrogen gas discharge system with regard to the formation of ESR centers in solid organic substances. A number of compounds including some of the purine and pyrimidine bases as well as certain amino acids have been exposed to X-rays, UV light, and thermal H atoms. It is the purpose of the present paper to demonstrate that for certain compounds the free radicals are produced by the vacuum UV light from the hydrogen gas discharge system, whereas for other substances the thermal hydrogen atoms are responsible for the radical production.

MATERIAL AND METHODS

Materials. Thymine, uracil, adenine, and DL-penicillamine (β,β-dimethylcysteine) were obtained from Sigma Chem. Corp., St. Louis, Missouri, and DL-leucine, DL-α-alanine, glycine, and glycyl-glycine were obtained from Nutritional Biochem. Corp., Cleveland, Ohio.

Samples were mainly prepared from polycrystalline powders. In some experiments where it was important to have a relatively well defined surface to volume ratio, particles with dimensions within a certain range were selected by a set of standard sieves. In these experiments the largest dimension of the particles varied from approximately 60 μ up to 500 μ.

In some experiments the substances were dissolved in distilled water and freeze-dried. It is expected that the freeze-drying process results in particles with a surface to volume ratio which is larger than for the other polycrystalline samples. Furthermore, it is reasonable to assume that this method of lyophilization increases the volume fraction of the amorphous phase.
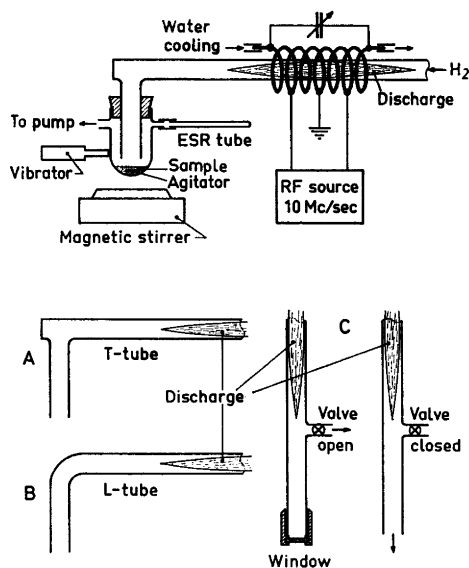
Fig. 1. A diagram of the most important parts of the hydrogen gas discharge system. The discharge tube C can be used with different types of windows. In that case the mechanical pump must be connected directly to the discharge tube.

The hydrogen gas discharge system. A diagram of the most important components of the hydrogen gas discharge system is presented in Fig. 1. Pure and dry hydrogen gas was pumped through a quartz discharge tube at a pressure of 0.3 to 0.4 mm Hg. The discharge was initiated and maintained by a radiofrequency source (10 Mc/sec). The powder samples were exposed to the discharge products in a glass tube to which an ordinary ESR tube was connected.

The discharge products include free hydrogen atoms as well as high-frequency UV light. No spectral analysis of the UV light has been performed, but the Lyman α-line with a wavelength of 1216 Å is known to be one of the main discharge products. This accompanying UV light can be reduced by introducing bends in the discharge system. In the present experiments the three different discharge tubes, shown in Fig. 1. A, B, and C, have been used in order to separate the discharge products.

UV irradiation. For UV irradiation the discharge tube without any bends, shown in Fig. 1 C, was used. Without windows the samples were exposed to all the discharge products. In the present experiments two types of windows were used. Thus, 2 mm thick windows of LiF or quartz could be adapted to the end of the discharge tube. The LiF window was obtained from Harshaw Chem. Co., Cleveland, Ohio.

It is evident that the windows stop the gaseous products including the thermal H atoms. Whereas the quartz window stopped UV light with wavelengths below 1800 to 2000 Å, the cut-off wavelength for high purity LiF is approximately 1040 Å. According to the manufacturer the transmission of the Lyman 1216 Å line is more than 50 %.

H atom exposure. The samples were exposed to thermal H atoms when discharge tubes without windows were used. The accompanying UV light was reduced by introducing bends in the discharge system. In the present experiments discharge tubes containing only one bend of approximately 90° were used. However, the shape of the tubes varied as shown in Fig. 1. In the T-shaped tube an appendix was introduced in order to reduce the reflection of UV light into the sample tube.

From Fig. 1 it appears that it is possible to reverse the gas stream (by exchanging the pump and the hydrogen gas reservoir) leaving all the essential parts of the discharge system unchanged. The purpose of such experiments is to expose samples positioned both downstream and upstream to the discharge itself. It is expected that the number of hydrogen atoms which reach the sample is greatly reduced in the upstream experiments whereas the accompanying UV light is independent of the direction of the gas stream.

Sample preparation. Polycrystalline samples of approximately 40 to 60 mg and freeze-dried samples of about 20 mg were used. The samples were stirred both mechanically and magnetically in order to expose all sides of the particles. The exposure times in the UV experiments were in the range from 5 to 40 min, whereas in the experiments with H atoms (the T-shaped tube) exposure times down to 1 sec resulted in readily observable ESR spectra for certain substances. After exposure the system was evacuated and the sample transferred by the mechanical vibrator to the ESR tube and then sealed off. The temperature during exposure was 295°K when not otherwise stated.

X-Rays. The X-irradiated samples were prepared in ordinary glass ESR tubes, evacuated to a pressure of 10^{-4} to 10^{-5} mm Hg for about 30 min, and then sealed off. They were irradiated with 220 kV X-rays to a dose of from 5×10^5 rad to 1×10^6 rad. The dose-rate was measured with an ionization chamber. The irradiation temperature was room temperature when not otherwise stated.

The ESR spectrometer. An X-band spectrometer with transmission cavity, 110 kc/sec modulation frequency, and crystal detection was used. The microwave frequency was measured with a wavemeter to an accuracy of about 1 Mc/sec. The magnetic field was measured with a proton resonance field meter.

The ESR measurements were carried out both at 77°K and at room temperature. The number of ESR centers was calculated by double integration of the first derivative spectra and comparison with reference samples. Anthracite carbon powder, calibrated against DPPH, was used as secondary standard.

RESULTS

A. Radicals induced by UV light and thermal hydrogen atoms. In the present experiments two compounds, glycyl-glycine and thymine, have been chosen to demonstrate the differences in radical production in the various discharge systems. The yields of radicals, given in relative units, are presented in Table 1. Large differences between the two substances are noticed and evidence will be presented below that the glycyl-glycine radicals are produced mainly by the UV light, whereas in the case of thymine the thermal hydrogen atoms are the source of radical production.

The UV light produced in a hydrogen gas discharge system is known to include the Lyman α-line with a wavelength of 1216 Å. This implies that, unless special precautions are taken, photons with an energy of 10.2 eV will reach the sample. This energy is sufficient to break the majority of chemical bonds and is also larger than the ionization potential for a number of sub-

Table 1. Yield of radicals in glycyl-glycine and thymine in different discharge systems.

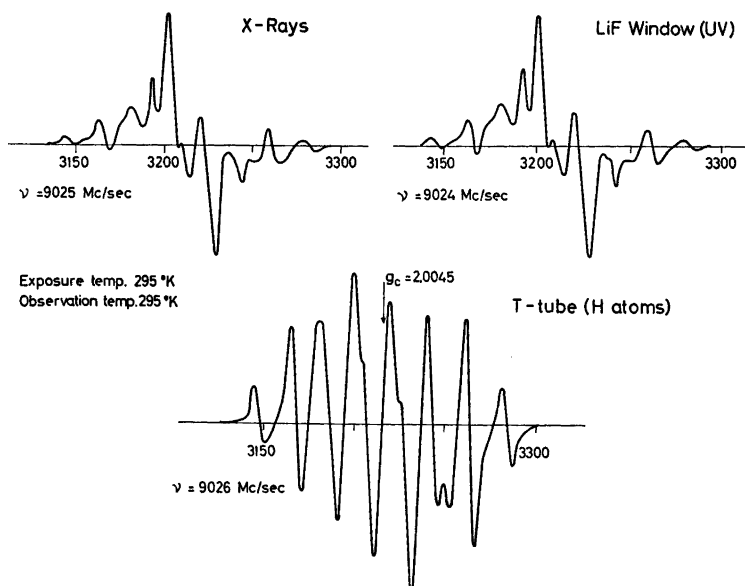| Discharge system	Radical yield in glycyl-glycine (Relative units)	Radical yield in thymine (Relative units)
Straight tube. No window	1	1
Staight tube. LiF window.	1/2	1/200
Straight tube. Quartz window	1/100	<1/10 000
L-shaped tube	1/20	1
T-shaped tube	1/1600	1

Fig. 2. The qualitative ESR spectra of thymine exposed to X-rays, vacuum UV light, and thermal hydrogen atoms. The spectra represent the first derivative of the absorption curves. The modulation amplitude is approximately 2 gauss. The *g*-value is calculated from simultaneous measurements of the magnetic field and the microwave frequency.

stances.[15] It is therefore expected that this high-frequency or vacuum UV light in many respects will yield radiation effects similar to those obtained with ionizing radiation.

In a straight tube (Fig. 1, C) all the discharge products are present. When windows are introduced, all the gaseous products are stopped whereas the UV light is transmitted, but more or less reduced according to the type of window used. Thus, with the quartz window only UV light with wavelengths above 1800 Å is transmitted, whereas the high-frequency UV light, including the Lyman α-line, is transmitted when the LiF window is used. The differences in radical yield (Table 1) demonstrate that the high-frequency UV light reaches the sample. It was found that the high-frequency UV light yielded ESR spectra in all substances studied. From the shapes of the spectra it appears that the same types of radicals are formed whether the origin is the vacuum UV light or ionizing radiation. Two examples are presented in Figs. 2 and 6, respectively. Quantitatively, it was found that the LiF window reduced the radical yield by about 50 % in glycine, alanine, and glycyl-glycine, whereas a large reduction was observed for thymine (see Table 1).

When bends are introduced in the discharge system, the UV light is reduced whereas the number of thermal H atoms seems to be almost unaffected. With the assumption that the UV light is responsible for the radicals induced in glycyl-glycine, it appears from Table 1 that an L-shaped tube reduced, but in no way eliminated, the UV light. This was ascertained in

experiments where the hydrogen gas was replaced by helium. In these experiments, where the reactive gaseous products were eliminated, radicals were induced in glycyl-glycine to the same extent as in the experiments with the hydrogen gas.

When a T-shaped discharge tube is used, the UV light is almost eliminated and the main radical source is the thermal hydrogen atoms. Consequently, it is suggested that the ESR spectrum observed for thymine (Fig. 2, bottom curve) is due to radicals formed by reactions between thermal hydrogen atoms and thymine molecules. The evidence in favor of this interpretation can be summarized as follows:

1. The qualitative ESR spectrum observed after exposure of thymine to the hydrogen gas discharge in the T-shaped tube is different from that induced by vacuum UV light and X-rays. This observation is in agreement with the results reported by Heller and Cole,[12] whereas both Herak and Gordy [10] and Holmes et al.[7] reported that the ESR spectrum they observed after exposure to the hydrogen gas discharge products was similar to that obtained for X-irradiated thymine.

In experiments with leucine, small qualitative differences were observed between the UV induced spectrum and that obtained with the T-shaped discharge tube (see Figs. 5 and 6). In similar experiments no differences were observed for penicillamine, whereas in the case of malonic acid the spectrum changed completely.

2. In Fig. 3 the dose-effect curves for radical production by the discharge products in the T-shaped tube are presented. It should be noted that in these experiments polycrystalline thymine with particle dimensions in the range 60 to 100 μ were used. The radical production is extremely large during the first seconds and the dose-effect curve starts to flatten off already after ap-
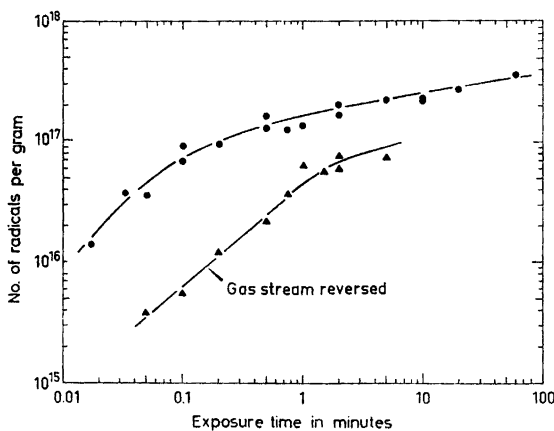

Fig. 3. Dose-effect curves for radical production in thymine by thermal hydrogen atoms. Polycrystalline thymine was exposed to the hydrogen gas discharge products in the T-shaped tube. The lower curve refers to experiments with the gas stream reversed. It should be noted that exposure times down to 1 sec were used. The exposure temperature was 295°K.
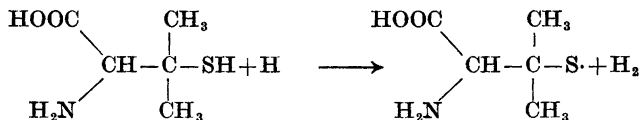
proximately 6 sec. This observation is in contrast to the UV experiments where exposure times of several minutes seem to be necessary in order to produce observable spectra.

3. In the present investigation experiments have been carried out with the hydrogen gas stream reversed. As mentioned above, this reversion of the gas stream will presumably not influence the accompanying UV light, but it is expected that the number of thermal H atoms which reach the sample will be reduced by a large factor. In accordance with this it appears from Fig. 3 that the dose-effect curve for upstream exposures is well below that obtained in the downstream experiments. The difference between the two curves is largest in the low dose range where no saturation effects influence the radical trapping. From the linear parts of the dose-effect curves it can be calculated that the radical production in the downstream experiments is about 18 times more efficient than with the gas stream reversed.

4. The quantitative results for thymine presented in Table 1 are in complete disagreement with the results for glycyl-glycine and consequently with the UV model.

Based on the present results it can be concluded that a hydrogen gas discharge system contains at least two products which readily produce radicals in organic solids. When discharge tubes with only one right angle bend are used both products participate in the formation of radicals. It was found that the substances can be divided into three groups. In the first group, which includes substances such as glycine, alanine, and glycyl-glycine, the radicals were formed by the vacuum UV light. In the second group, containing leucine, penicillamine, and malonic acid, both the UV light and the thermal hydrogen atoms contributed to the formation of the observed radicals. Finally, in the third group, where thymine and uracil can be found, the H atom-induced radicals are completely dominating.

B. *The types of H atom-induced radicals.* It is of interest to elucidate the mechanisms whereby the thermal hydrogen atoms produce free radicals. One step in this direction would be the identification of the induced radicals. This is usually very difficult as long as polycrystalline samples are used. However, in the case of the thiol penicillamine the observed resonance pattern is identical to that found for X-irradiated samples. Quite good evidence has been presented [16] that this resonance is due to a sulfur radical with the unpaired spin density mainly in a $3p$ orbital on the sulfur atom. Consequently, in this case the underlying mechanism is presumably an abstraction reaction:

$$
\begin{array}{ccc}
HOOC \diagdown & CH_3 & \\
& \mid & \\
& CH-C-SH+H & \\
H_2N \diagup & \mid & \\
& CH_3 &
\end{array}
\longrightarrow
\begin{array}{cc}
HOOC \diagdown & CH_3 \\
& \mid \\
& CH-C-S\cdot+H_2 \\
H_2N \diagup & \mid \\
& CH_3
\end{array}
$$

Similar reactions may also take place in the case of other saturated molecules.

The resonance spectrum observed for thymine, exposed to thermal hydrogen atoms (Fig. 2, bottom curve), consists mainly of 8 lines centered around a g-value of 2.0045. Additional hyperfine lines are also observable in the middle

of the spectrum. This latter hyperfine splitting depends upon the observation temperature as well as the exposure time (the dose) as shown in Fig. 4. Thus, when the dose is small and the observation temperature is that of liquid nitrogen, the splitting of the middle lines can be measured to about 9 gauss. The overall splitting is 139 gauss and the splitting between the two outermost lines on each side is 20.6 gauss. It has been suggested that only one type of radical (I) is responsible for this resonance.[10,12,17]

(I)
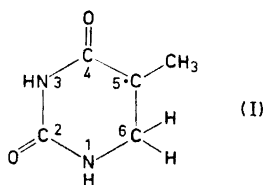
The origin of the hyperfine splitting is the β-protons in the methyl and methylene groups. The upper spectrum in Fig. 4 suggests the following splitting constants; a $(CH_3)=20.6$ gauss, a_1 $(CH_2)=34.1$ gauss, and a_2 $(CH_2)=43.1$ gauss. This implies that the two methylene protons are not equivalent with regard to the unpaired spin density as suggested by Heller and Cole.[12] Based on these splitting constants, a 16 line spectrum appears where the 12 middle lines form 4 groups each consisting of 3 lines. The splitting within each group is small and the three lines will partly coalesce into a broad line with a poorly resolved hyperfine splitting. Consequently, the overall appearance of the signal in powder samples will be an 8-line spectrum with some broadening and hyperfine splitting for the 4 middle lines.

In Fig. 4 it appears that the hyperfine splitting in the middle becomes smeared out with increasing exposure time and dose. The possibility that this is due entirely to dipolar broadening from the increased radical concentration seems to be a remote one (see below), and the most reasonable explanation is that other radicals are formed.

The above experimental results seem therefore to indicate that the main reaction between a thermal hydrogen atom and a thymine molecule is an addition of the hydrogen atom to carbon atom 6 in the pyrimidine ring. It is of interest to note that in the X-irradiated and UV-exposed samples the thymine spectra appear to be composite, and the above discussed thymidyl radical accounts for approximately 25 % of the resonance pattern at room temperature. In conclusion; thermal hydrogen atoms may react with organic solids either by abstracting from or adding to the substance a hydrogen atom.

C. The distribution of radicals. In the experiments with the thermal hydrogen atoms the physical form of the samples seems to be of greatest importance. Thus, in the case of thymine it was found that the yield of radicals in a freeze-dried sample was larger than that for a polycrystalline sample by a factor of approximately 4. Furthermore, for the amino acid penicillamine very few radicals were observed for a polycrystalline sample, whereas a large spectrum appeared when the more fluffy freeze-dried material was used. Since the surface to volume ratio is larger for a freeze-dried sample, the above
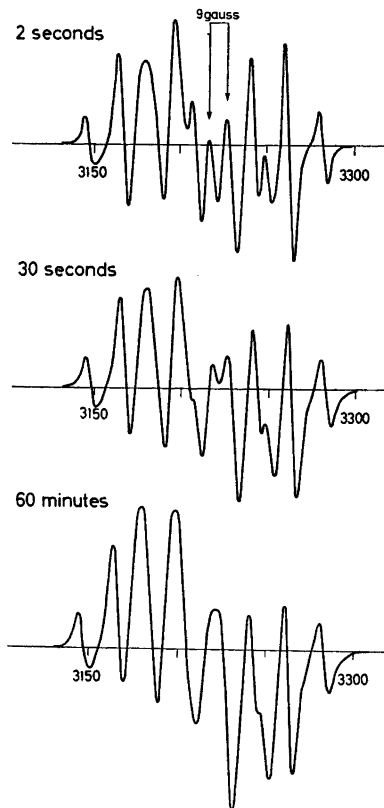
Fig. 4. Variation in the qualitative ESR spectrum of thymine with increasing exposure time and dose of hydrogen atoms. The exposure temperature was 295°K, whereas the observation temperature was 77°K.

observations suggest that the thermal hydrogen atoms can only penetrate the surface layer of the particles.

It is possible to arrive at a rough estimate of the radical distribution within the crystallites from the experiments with thymine presented in Fig. 4. It appears that the line width, as measured between maximum slopes, increases almost linearly with the radical concentration. The line broadening for the two outermost lines on each side was measured to approximately 0.35 gauss per 1×10^{17} spins/g.

Dipolar broadening of ESR lines has been treated theoretically by Kittel and Abrahams [18] for single crystals, and has been adapted to polycrystalline samples by Wyard.[19] The increase in line width with the radical concentration is given by the following formula:

$$\varDelta H = 5.4 \times 10^{-20} \ N$$

where N is the number of radicals per cm^3. If we assume that the observed increase in line width is entirely due to dipolar broadening, the above formula leads to a radical concentration of approximately 5×10^{18} spins/g. This implies that the radicals are not distributed evenly throughout the crystallites. If

we assume that the radicals are concentrated to a surface layer and that the particles are spherical (radius R) the thickness of this layer (ΔR) is given by:

$$4/3\ \pi\ R^3 \times 10^{17} = 4\ \pi\ R^2\ \Delta R \times 5 \times 10^{18}$$
$$\Delta R = R/150$$

In the present experiments R was in the range 25 to 50 microns which implies that ΔR is of the order of 2000 to 3000 Å.

Since the radicals induced in a solid substance by thermal hydrogen atoms seem to be localized mainly in the surface layer of the particles, they will also be accessible to diffusible gases. In accordance with this it was found that when a thymine sample was exposed to air, subsequent to H atom bombardment, the induced radicals rapidly combined with oxygen and disappeared in combination reactions. In the case of leucine the oxygen-induced product was much more stable (Fig. 5). Thus, when this amino acid was exposed to thermal hydrogen atoms, a well resolved 8-line spectrum appears which rapidly is changed into an assymmetric line when air is admitted. When the observation temperature is that of liquid nitrogen (Fig. 5, middle curve) the oxygen-induced radical exhibits axial symmetry with $g_\perp = 2.0030$ and
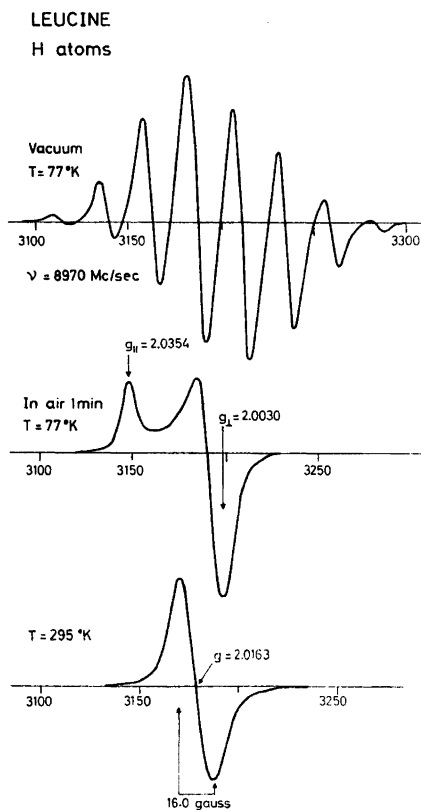

Fig. 5. Effect of oxygen on the hydrogen-induced radicals in leucine. Polycrystalline leucine was exposed to thermal hydrogen atoms at room temperature. After exposure the sample was evacuated and sealed off. After the first measurement at 77°K the sample was brought to room temperature and opened to air for one minute. The middle spectrum was that observed at 77°K, whereas the bottom resonance was that obtained when the observation temperature was raised to 295°K. The differences between the two bottom spectra are due only to the observation temperature.

$g_{||} = 2.0354$ (20). These g-values are close to those observed by Wyard and Smith[21] for HO_2 radicals, and by Sullivan and Koski[22,23] for the methoxy and ethoxy radicals. It should be noted that the latter authors open up the possibility that the responsible radicals are the corresponding peroxy radicals. When the observation temperature is raised to room temperature (Fig. 5, bottom curve), a single line with $g = 2.0163$ and a width of 16 gauss was observed. The spectral variation with the observation temperature revealed in Fig. 5 is reversible. The lack of hyperfine structure and shift in the g-value from that of the free spin suggests that the responsible radical is a peroxy radical.[24]

The rapid effect of oxygen in the case of H-induced radicals in leucine is similar to that previously reported by Snipes and Schmidt.[13] However, a difference in the effect of oxygen between samples exposed to X-rays and to the hydrogen gas discharge products does not necessarily imply that the radicals are produced by the thermal H atoms, since UV-induced radicals
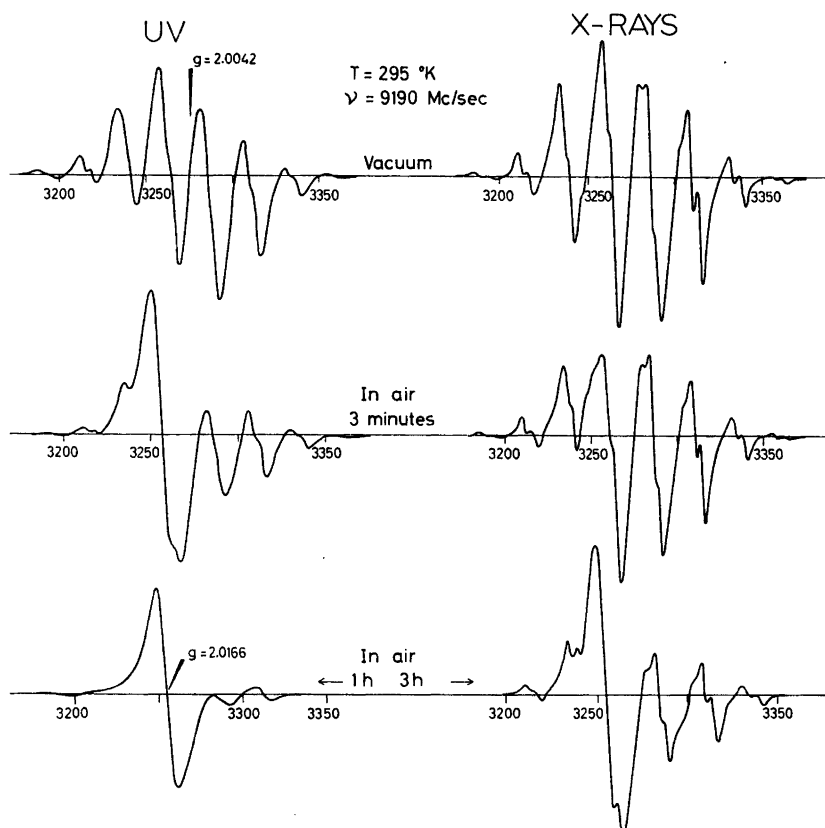

Fig. 6. The qualitative ESR spectra of leucine exposed to vacuum, UV light and X-rays. The exposure as well as the observation temperature was 295°K. Polycrystalline leucine was used.
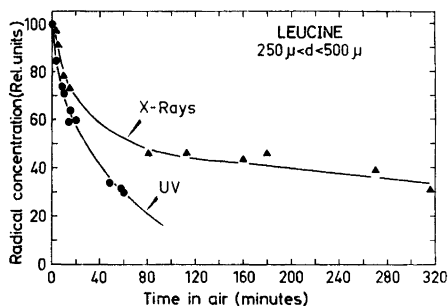
Fig. 7. The effect of oxygen on the number of radicals in leucine. The two curves refer to X-ray and UV-induced radicals. The yield data include all types of radicals, both leucine radicals as well as peroxide radicals. Polycrystalline leucine was used. The diameter of the particles d (or the largest dimension) was in the range from $250\ \mu$ to $500\ \mu$.

also seem to be localized near the surface of the particles. This is clearly demonstrated for leucine in Figs. 6 and 7. In the first place, it can be noted that the X-ray induced resonance is similar to that induced by the UV light which penetrates the LiF window. However, the distribution of radicals in the two samples seems to be different. This is apparent already from the two top spectra in Fig. 6. Even though the samples responsible for the two spectra contain almost the same number of radicals, the X-ray-induced resonance exhibits a more resolved hyperfine pattern. This indicates that the UV-induced radicals are concentrated to a surface layer where the concentration reaches such values that dipolar broadening influences the hyperfine pattern.

When air subsequently is admitted to the leucine samples it appears from the results in Figs. 6 and 7 that the reactions with oxygen are much faster and more extensive in the case of the UV-induced radicals. It should be emphasized that both samples contain particles with diameter in the range from 250 to 500 μ, and the results can therefore be compared directly.[25]

DISCUSSION

The results presented in the present paper demonstrate that a hydrogen gas discharge system contains two different products which can produce free radicals in solid organic substances. Thus, well resolved ESR spectra were observed for a number of substances such as thymine, uracil, leucine, penicillamine, and malonic acid in experiments under conditions where either the UV light or the thermal hydrogen atoms were the dominating discharge product. The two substances thymine and glycyl-glycine appear to be well suited for experiments intended to distinguish between the different discharge products. Thus, in glycyl-glycine the radicals are formed almost exclusively by the vacuum UV light, whereas thymine reacts readily with thermal hydrogen atoms, but is quite resistant to radical formation by UV light and X-rays.

The UV light in a hydrogen gas discharge system contains high energy photons (the Lyman α-line has a quantum energy of 10.2 eV). Consequently, the UV light which is always present in discharge experiments is capable of producing radicals in much the same way as ionizing radiation. The present experiments show that UV light reaches the sample even when bends are introduced in the discharge system. Since right angle bends (L-shaped discharge

tubes), which are not sufficient to eliminate the UV light, have been used it is possible that a larger or smaller fraction of the observed radicals was induced by the UV light. It was found in the present experiments that a discharge tube with an appendix (a T-shaped tube) reduced the accompanying UV light sufficiently.

The present results may be of interest with regard to the mechanisms for radical formation and stabilization. When ionizing radiation is used a large variety of primary species are induced. Some of these disappear rapidly, whereas others become trapped as such, or become involved in reactions which lead to the formation of secondary radicals. It is evident that when the ESR technique is used after irradiation we observe only those radicals that for certain reasons are trapped. It may be expected a priori that the distribution of radical traps within a solid is homogeneous. However, X-ray experiments with protein particles with different dimensions [26] seem to indicate that even under conditions where the initial energy absorption is homogeneous, the concentration of the trapped radicals seems to increase towards the surface of the particles.

When the source of radical production is the products in a gaseous discharge it is expected that also the initial events are localized to the surface layer of the particles. Consequently, when the surface to volume ratio increases, as for example by freeze-drying, the yield of trapped radicals increases. The experiments with thymine seem to indicate that the thickness of the surface layer influenced by the thermal hydrogen atoms is of the order 0.2 to 0.3 μ. This implies that the thermal hydrogen atoms may penetrate a layer of a few hundred molecules before they react.

The experiments with leucine and the oxygen effect seem to demonstrate the variation in the distribution of the trapped radicals formed by the different types of radiation or exposure. Even though the concentration of the X-ray-induced radicals exhibits a tendency to increase towards the surface of the particles, the radicals formed by the discharge products seem to be confined to the surface layer only. The results show that the surface layer influenced by the UV light is much thicker than that penetrated by the thermal hydrogen atoms. In spite of these differences it appears unlikely that the oxygen effect can be used to differentiate between UV- and H-induced radicals.

Hydrogen atoms are usually formed when a system is exposed to ionizing radiation. Consequently, one of the main purposes for using thermal hydrogen atoms is the possibility of studying certain aspects of the radiation picture without introducing disturbing effects from the other radiation products. The present experiments support the conclusion by Herak and Gordy [10] and by Cole and Heller [8,9,12] that thermal hydrogen atoms react with aromatic substances such as thymine and some of the other nucleic acid bases by an addition reaction, whereas in the case of saturated molecules such as penicillamine, leucine, malonic acid and others the radicals are formed by abstraction reactions. In some recent experiments we found that the addition reaction is temperature dependent. Thus, if thymine is exposed to thermal hydrogen atoms below approximately 160°K, no radicals are formed. Experiments are now in progress where the addition reaction is studied under conditions where the abstraction takes place concurrently.

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