Positron Lifetimes in γ-Irradiated Eicosane and Polyethylene

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The positron lifetimes in a γ-irradiated single crystal of *n*-eicosane and amorphous polyethylene have been measured at -78 °C in a vacuum. The lifetime, τ_2, of the long-lived component decreases upon irradiation in both systems, and the increase in the annihilation rate, λ_2, is proportional to the concentration of free radicals. Assuming that the decrease in τ_2 is entirely due to the reaction of orthopositronium (*o*-Ps) with free radicals, the diffusion constant of *o*-Ps has been estimated to be $D=0.58$—1.75×10^{-5} cm^2 s^{-1}. The intensity, I_2, of the long-lived component decreases markedly in *n*-eicosane, levelling off at about 20%. I_2 in polyethylene does not decrease upon irradiation. Some possible explanations are given.

It is a well-known fact that the lifetime spectra of positrons in solids are influenced both by the chemical properties and by the physical structure.[1] A fraction of the positrons can capture an electron from the surrounding medium and form a bound state called "positronium". The positronium with a total spin number of $S=0$ is called the "parapositronium" (*p*-Ps). The lifetime of *p*-Ps is small ($\tau_p=0.125$ ns), and usually we cannot distinguish, with our conventional time-analyzer, this lifetime component from that of free positrons.

The positronium with a total spin number of $S=1$ is called the "orthopositronium" (*o*-Ps). The lifetime of *o*-Ps is 140 ns in a vacuum, but it is much shortened as a result of the following processes: 1) pick-off quenching, 2) conversion quenching, and 3) chemical quenching.

In a condensed medium, a positron in *o*-Ps has an opportunity to sample an electron in the medium and be annihilated into two gamma quanta. This is called "pick-off quenching." In general, the lifetime of *o*-Ps becomes shorter in a smaller free volume, because, in a smaller free volume, the positron in *o*-Ps has a larger opportunity to sample electrons in the medium. This phenomenon is called the "free volume effect" on *o*-Ps lifetimes.

If the medium contains paramagnetic species, *o*-Ps may be converted to *p*-Ps upon collision with them. The lifetime of *o*-Ps is also reduced by this process. This is called "conversion quenching."

If there are molecules which are reactive toward *o*-Ps to form a positronium compound, the lifetime of *o*-Ps is also reduced, because in a positronium compound the positron has a large opportunity to be annihilated with electrons in the compound. This is called "chemical quenching."

The formation probability of positronium, on the other hand, ranges from 0 to about 50%, depending on the substance. The so-called "Ore model" provides a simple method to estimate the formation probability. This model states that positronium formation is predominant in the region of positron energies from E (the energy of excitation of the first electron level of molecules) to $V-6.8$ eV (V is the ionization potential of molecules, and 6.8 eV is the dissociation energy of positronium). This model, however, must be modified in a condensed phase because of the affinity of the medium to electrons, positrons, and positronium. However, even without these complicating factors, there are cases where the formation of positronium is inhibited due to: 1) the process of the inelastic slowing down of positrons, as a result of which positrons quickly go below the Ore gap and 2) the process of the capture of positrons in the energy region of the Ore gap. Furthermore, in certain circumstances it is possible that positronium is chemically quenched, while it is not thermalized; in this case, the apparent formation probability of positronium may be decreased.

All of the above processes can be affected by radiation-induced changes in solid materials. It has indeed been reported by the present authors[2] and by others[3] that the positron lifetime spectra in various organic solids are altered in various ways by γ-irradiation.

In this paper we wish to report the results of our positron lifetime measurements in γ-irradiated *n*-eicosane (n-$C_{20}H_{42}$) and polyethylene. The former has been obtained in the form of single crystals, while the latter is known to contain many amorphous regions and defects. Positron annihilation studies in irradiated polyethylene have been reported by Chandra *et al.*[3a] and J. H. Green *et al.*;[3c] however, since their studies were carried out with samples in air at room temperature, many complex radiation chemical changes should have been taking place and it is difficult to interpret the changes in the lifetime spectra. In order to avoid such complexity, it is advantageous to carry out γ-irradiation and lifetime measurements at a lower temperature *in vacuo*.

Experimental

Sample Preparation. About 15 μCi of ^{22}NaCl was deposited on two single crystals of *n*-eicosane. They were positioned face to face on the deposited side and then placed in a glass ampoule which was subsequently sealed off in a vacuum.

Polyethylene, which had been supplied and named "Takathene" by the Takasaki Radiation Chemistry Research Establishment, JAERI, is the product of the high-pressure radiation-induced polymerization of gaseous ethylene; therefore, it is expected to contain no impurities. This polymer was pressed in the form of two tablets ($10\phi \times 3$ mm), which were then prepared as a sample for lifetime measurement in the same manner as in the case of *n*-eicosane.

Irradiation and Measurements. Both lifetime measurements and γ-irradiations were carried out at −78 °C, except for those in which the samples were irradiated and measured at room temperature for the sake of comparison.

The lifetime measurements were carried out with a conventional time-analyzer using delayed coincidence technique as has been reported previously.[2] The resolution of the, time-analyzer was 0.34 ns at full width at half maximum of the Co-60 prompt peak for the Na-22 energy selection. It took a run of about 2 days to obtain a single spectrum with a total of approximately 5×10^5 counts. The peak-to-background ratio was greater than 10^4. The lifetime spectra were analyzed by the method of least squares to determine the intensity, I_2, and the lifetime, τ_2, of the long-lived component. The intensity was calculated as the ratio of the area of the long-lived component to that of the total area under the distribution curve.

The concentration of free radicals was measured with an ESR spectrometer (JEOL PE-3X) using a calibrated amount of DPPH in a benzene solution frozen at −78 °C as a standard.

Results and Discussion

Positron Lifetimes in Non-irradiated Samples. The lifetime spectra in *n*-eicosane and polyethylene could be resolved into two components. The mean lifetimes and intensities for non-irradiated samples are given in Table 1. Each datum is the average of at least three measurements carried out under different instrumental conditions—*i.e.*, with different window widths of the wide-channel energy selection and with different time widths per channel (0.05—0.10 ns/channel).

TABLE 1. POSITRON ANNIHILATION DATA FOR *n*-EICOSANE AND TAKATHENE BEFORE IRRADIATION

	τ_1 (ns)	τ_2 (ns)	I_2 (%)
n-Eicosane (−78 °C)	0.124±0.02	1.15±0.05	52.7±1.5
n-Eicosane (0 °C)	0.28 ±0.03	1.32±0.02	30.4±0.8
Takathene (−78 °C)	0.19 ±0.02	1.71±0.05	29.3±1.0
Takathene (0 °C)	0.36 ±0.04	2.62±0.05	19.2±3

It has often been reported that there are two *o*-Ps components in most polymeric systems, the longer component being attributed to *o*-Ps annihilation in amorphous regions and the shorter one to that in crystalline regions.[4] We could, however, observe only one *o*-Ps component in Takathene. This is natural in view of the special features of this polymer: it has been postulated from the X-ray diffraction and NMR studies of Takathene that the crystal size is small (130—160 Å) and that, moreover, many defects are included in the crystalline regions.[5] In such a structure, *o*-Ps, even if produced in the crystalline regions, may quickly diffuse out to non-crystalline regions or be trapped in crystal defects, since most *o*-Ps has, at the time of its production, a considerable energy above thermal and, therefore, can move a substantial distance. This situation is analogous to the escape of *o*-Ps from inside crystal particles of metal oxides to their surfaces.[6] We will, therefore, assign the long-lived component in Takathene to the annihilation of the *o*-Ps which is thermalized in the non-crystalline regions.

τ_2 in Takathene is larger than that in *n*-eicosane. This is natural in view of the free volume effect, because the density of *n*-eicosane is larger than that of amorphous polyethylene.

I_2 in *n*-eicosane and Takathene is larger at −78 °C than at 0 °C. Since we have not measured the positron lifetimes at temperatures between −78 and 0 °C, it is not clear whether this is connected with the "phase transition effect" on positron lifetimes which has often been reported for various materials.[7]

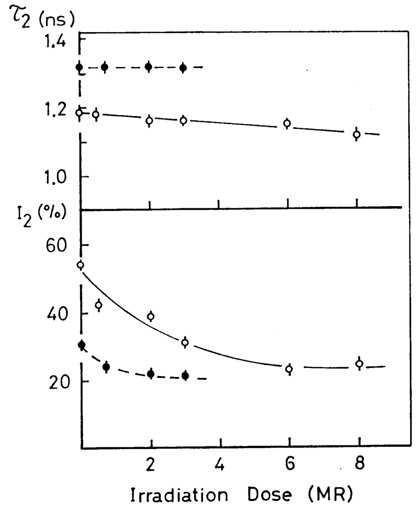

Fig. 1. I_2 and τ_2 in *n*-eicosane at −78 °C (○) and at a room temperature (●) as a function of the dose of γ-irradiation. The vertical bar at each point shows the statistical error of the coincidence counting rate.

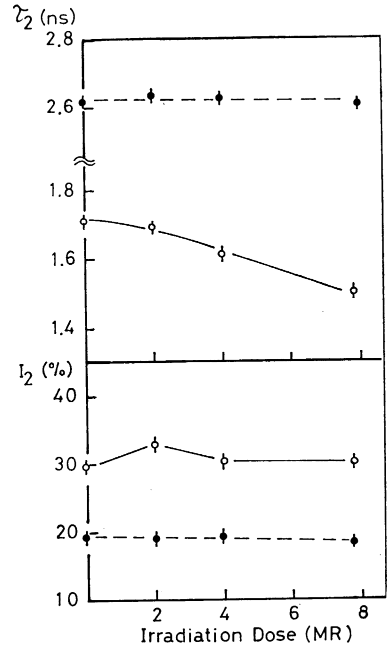

Fig. 2. I_2 and τ_2 in amorphous polyethylene at −78 °C (○) and at a room temperature (●) as a function of the dose of γ-irradiation.

Effect of γ-Irradiation on τ_2. The variations in τ_2 and I_2 are shown in Figs. 1 and 2 as a function of the γ-ray dose. τ_2 decreases upon γ-irradiation in both systems, although the decrease seems smaller in *n*-eicosane than in polyethylene. This may, however, be only apparent, because the radiation yield of free radicals (mainly alkyl radicals $-CH_2CHCH_2-$) in *n*-eicosane is approximately one-third that in polyethylene under the present conditions. Moreover, if we plot $\Delta\lambda_2=\lambda_2-\lambda_2^0=1/\tau_2-1/\tau_2^0$ (where λ_2^0 and τ_2^0 are the annihilation rate and the lifetime in a non-irradiated sample respectively) against the spin concentration, it is expressed by a linear relation, as is shown in Fig. 3. From this result, we may assume that the decrease in τ_2 is the result of *o*-Ps reaction with free radicals:

$$o\text{-Ps} + \mathrm{R} \xrightarrow{k[\mathrm{R}]} \mathrm{PsR} \longrightarrow 2\gamma \qquad (1)$$

The fact that τ_2 does not vary when the sample is irradiated at room temperature also supports this assumption, because the spin concentration in samples irradiated at room temperature is far smaller than in those irradiated at −78 °C.

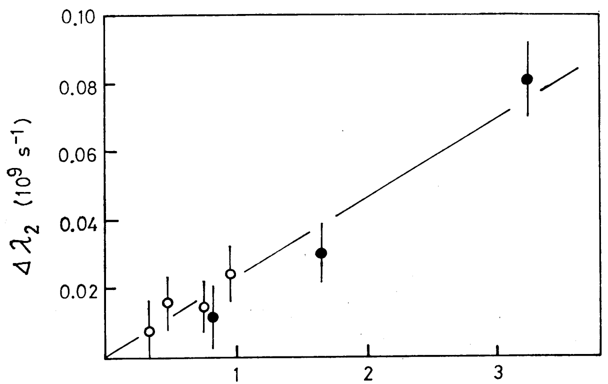

Fig. 3. The increase in the annihilation rate of *o*-Ps ($\Delta\lambda_2=\lambda_2-\lambda_2^0$) in *n*-eicosane (○) and amorphous polyethylene (●) as a function of the concentration of free radicals.

If the observed decrease in τ_2 is entirely due to the reaction of *o*-Ps with free radicals, the rate of Reaction 1 can be calculated to be;

$$k = 0.22\times10^{-11} \quad \mathrm{cm^3 \cdot s^{-1} \cdot spin^{-1}}$$

This is more than a factor of ten smaller than those for *o*-Ps reactions with various acceptors in organic liquids (0.1—10×10^{-10} cm^3 s^{-1} molecule^{-1}), in which the reaction is believed to be controlled by the diffusion of *o*-Ps.[8] Assuming that the mobility of *o*-Ps in the present substances can also be described in terms of diffusion, the following Smolkovskii formula is given:

$$k = \omega 4\pi(r_{\mathrm{Ps}}+r_{\mathrm{R}})(D_{\mathrm{Ps}}+D_{\mathrm{R}}) \qquad (2)$$

where r is the radius, D is the diffusion constant, and ω is the probability factor for the reaction. In applying Eq. (2) we take $r_{\mathrm{Ps}}=1$ Å, $r_{\mathrm{R}}=1$—2 Å, $\omega=1$, and $D_{\mathrm{R}}\ll D_{\mathrm{Ps}}$. The latter assumption is based on the fact that free radicals can be regarded as immobile in the time scale of the lifetime of *o*-Ps. We thus obtain:

$$D_{\mathrm{Ps}} = 0.58-1.75\times10^{-5} \quad \mathrm{cm \cdot s^{-1}}$$

This value is as large as that obtained from the reaction of *o*-Ps with DPPH in solid pyridine at −78 °C.[9] It is more than one-third smaller than those previously reported for metal oxides ($\gtrsim 6\times10^{-5}$ cm^2 s^{-1}).[6] However, since the diffusion constants in metal oxides were calculated from the intensity of *o*-Ps or *p*-Ps which has diffused from inside crystal particles to their surfaces, they have been averaged over all the energy spectrum of Ps and therefore, must be larger than those for the thermalized Ps. The fact that our diffusion constant is smaller than those in organic liquids, but is close to those in other solids, supports our assumption that thermalized *o*-Ps can react with free radicals. It must be noted, however, that we have taken $\omega=1$ in Eq. (2), assuming that every encounter of *o*-Ps with free radicals leads to compound formation or conversion quenching. Our diffusion constant is, therefore, a lower limit to the real one. We may conclude either that the mobility of *o*-Ps is small ($\omega=1$) or that the reactivity of *o*-Ps with alkyl radicals is small ($\omega\ll1$).

It must be noted that our diffusion constant is far smaller than those given by Gol'danskii *et al.*,[10] who also applied the Smolkovskii formula for the reaction rate of *o*-Ps with O_2 in solid cyclohexane ($D=1.2\times10^{-3}$ cm^2 s^{-1}) and solid benzene ($D=0.7\times10^{-3}$ cm^2 s^{-1}) at −196 °C, assuming that $\omega=1$. One possible explanation for this discrepancy is that, in solidified cyclohexane and benzene, thermalized *o*-Ps exists in vacancies at the grain boundaries of the polycrystals. Since O_2 molecules may also be selectively concentrated in the grain boundaries, *o*-Ps feels in reality a much larger concentration of O_2 than that averaged over all the volume of the substance. The diffusion constants calculated using the averaged O_2 concentration should be larger than the real ones. Detailed investigations will be required to confirm this, but it may be of great importance to consider in what domain of substances thermalized *o*-Ps exists and how it migrates in it.

Effect of γ-Irradiation and Thermal Annealing on I_2. I_2 decreases upon irradiation in *n*-eicosane and levels off at a value of about 20% (Fig. 1). It is interesting to note that the room temperature value of I_2 also decreases and levels off at 20%. It is expected that

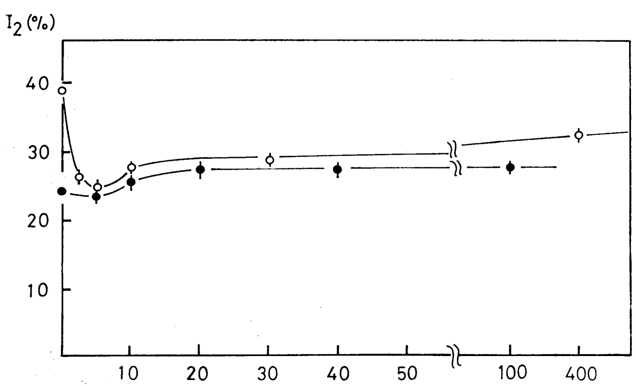

Fig. 4. Effect of thermal annealing at 30 °C on the intensity I_2 in *n*-eicosane irradiated to 2 MR (○) and 8 MR (●).

there is some threshold in the mechanism of the inhibition of thermalized *o*-Ps formation.

I_2 in irradiated *n*-eicosane varies upon thermal annealing, as is shown in Fig. 4. When *n*-eicosane, irradiated to 2 MR, is thermally annealed at 30 °C, I_2 decreases conspicuously to about 20% at first and then increases only slightly. However, in *n*-eicosane irradiated to 8 MR—*i.e.*, to a dose at which the decrease in I_2 levels off at -78 °C, the change due to thermal treatment is small, although it shows a similar tendency. This means that some structural and/or chemical changes which occur after the heat treatment are responsible for the initial decrease in I_2. It may be that, at the dose of 8 MR, such changes have already taken place to a degree sufficient to reduce I_2 to its lowest value and that further heat treatment does not induce any further change in I_2. There are several possibilities to be noted as such changes; the redistribution of free radicals, the conversion of the alkyl radical to the allyl radical $(-CH{=}CH{-}\dot{C}H{-}CH_2-)$, *etc.* It remains to be studied which of these possibilities holds true.

TABLE 2. EFFECT OF THERMAL ANNEALING ON τ_2 AND I_2 IN AMORPHOUS POLYETHYLENE

Conditions	τ_2(ns)	I_2 (%)
After irradiation of 8 MR at -78 °C	1.50 ± 0.02	29.3 ± 1.0
Annealed at 0 °C for 1 hr	1.41 ± 0.02	28.8 ± 1.1
Further annealed at 28 °C for 2.5 hr	1.53 ± 0.04	32.3 ± 0.8
Further annealed at 50 °C for 2.5 hr	1.51 ± 0.03	34.5 ± 1.5
Further annealed at RT for 800 hr	1.50 ± 0.02	33.2 ± 1.5

Contrary to the case of *n*-eicosane, I_2 in polyethylene does not decrease upon irradiation at -78 °C, and when thermally treated, it increases only slightly (Fig. 2 and Table 2). This is to be expected because the polyethylene used in the present experiment is quite amorphous, and the structure change due to irradiation or thermal treatment does not affect the positronium formation process as much as in crystalline *n*-eicosane.

Several explanations are possible for the observed decease of I_2 in *n*-eicosane both during γ-irradiation at -78 °C and during thermal treatment. Whatever the explanation may be, however, it must explain (1) the existence of a limit in I_2 reduction, (2) the significant I_2 reduction in annealed *n*-eicosane, and (3) the fact that γ-irradiation is ineffective in reducing I_2 in amorphous polyethylene. One possible explanation is the reaction of energetic *o*-Ps. It is expected that energetic *o*-Ps is rapidly thermalized in amorphous polyethylene by giving its energy to the vibration of molecular chains. Thus, in polyethylene energetic *o*-Ps migrates only a short distance before it is thermalized and has little chance to undergo reaction with acceptors such as free radicals. In crystals of *n*-eicosane, energetic *o*-Ps may migrate a significant distance before thermalization and thus may be able to undergo reaction. It is interesting to recollect in this connection the work by O. Mogensen *et al.*,[11] who showed that positronium moves in a fine crystal of ice as a Bloch wave and that it is rapidly localized in defect sites if such exist in the crystal. They suggested that a higher degree of order in the solid phase will enhance the Ps transport and lead to a stronger interaction. In *n*-eicosane, *o*-Ps may similarly be rapidly transported and localized in defect sites upon collision with them, and since the defect sites are paramagnetic in this case, energetic *o*-Ps may be quenched by the latter, resulting in the reduction of I_2.

If the above explanation is correct, it follows that there is essentially no difference between the mechanism by which τ_2 in *n*-eicosane and polyethylene is shortened and the mechanism by which I_2 in *n*-eicosane is reduced by the irradiation; the reaction of energetic *o*-Ps with free radicals reduces I_2, while the reaction of thermalized *o*-Ps shortens τ_2.

The limits in I_2 reduction might be attributed either to a "cage effect," which confines Ps with an energy below a certain thereshold in a limited region of the substance, or to the presence of some resonance in the mechanism by which *o*-Ps is transported in the crystal of *n*-eicosane.

We cannot, of course, exclude other explanations for the I_2 reduction. The existence of the paramagnetic sites might enhance the direct annihilation of positrons either by narrowing the effective Ore gap or by rapidly moderating the positron energies below the gap. Paramagnetic sites might also capture positrons and form positron compounds, thus inhibiting positronium formation. It seems difficult, however, to explain in terms of these processes why I_2 is not decreased in amorphous polyethylene by the irradiation, while it is decreased in *n*-eicosane.

Our present study involves many problems, and most of them are scarecely understood at present. Further extensive study is needed, but the problems raised in this work will be of importance in understanding the fundamental processes of positronium chemistry in organic solids.

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