



# Ortho-para spin conversion of Ps by paramagnetic O<sub>2</sub> dissolved in organic compounds

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**Abstract.** The *o*-Ps mean lifetime value in liquids decreases in the presence of the paramagnetic oxygen molecules via the *ortho-para* conversion process. This effect was observed for several organic samples composed of carbon and hydrogen atoms differing in the arrangement of atoms forming the molecule, e.g. *n*-alkanes, alcohols, branched isomer of alkane, cycloalkane. The usually observed tendency of the *o*-Ps lifetime value to be an increasing function of temperature (in the case of measurements performed in vacuum) changes to a decreasing one in the presence of O<sub>2</sub> dissolved in the sample. The difference between the *o*-Ps lifetimes measured in samples in vacuum and in the presence of O<sub>2</sub> increases with the distance from the melting point. The *ortho-para* constant rate  $\lambda_{\text{conv}}$  was estimated to be  $\sim 130 \mu\text{s}^{-1}$  at 300 K for three compounds investigated.

**Key words:** alcohols • cyclohexane • isooctane • *n*-alkanes • *ortho-para* conversion • paramagnetic molecule

## Introduction

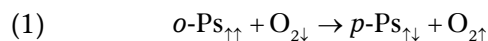
Interactions of Ps trapped in a cavity with the surrounding molecules in organic media in the presence of air can occur in different ways [1–4]:

- conversion due to paramagnetic molecules (e.g. NO, O<sub>2</sub>);
- oxidation by electron transfer, leaving a bare positron;
- formation of a positron compound.

In this work, special attention will be paid to the first-mentioned process. The chosen conditions of the experiment allowed us to attribute the observed effect to the presence of paramagnetic oxygen molecules (from the air) dissolved in the sample only. We assume that as a result of a Ps collision with a molecule (M) or an atom, the spins of the particles forming the positronium atom may be changed, e.g. the conversion of *o*-Ps into *p*-Ps and *vice versa* may occur. The only requirement for spin transition  $^3\text{S}_1 \leftrightarrow ^1\text{S}_3$  is that the M has unpaired electrons [5], and just the O<sub>2</sub> contained in the air has unpaired electrons. Taking into account the magnetic quantum number  $m$  ( $m_{p\text{-Ps}} = 0$ ,  $m_{o\text{-Ps}} = -1, 0, 1$ ), and considering that the lifetime of a singlet positronium state is short (compared to the lifetime of a triplet state), one can assume that the significance of *para-ortho* conversion is marginal. As a result of the *ortho-para* conversion in the presence of oxygen molecules, which can be described by the equation:

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the *o*-Ps lifetime value measured in positron annihilation lifetime spectroscopy (PALS) experiments is reduced. Generally the measured *o*-Ps lifetime ( $\tau_3$ ) is taken as a reversal of decay constant, and in the case of short lifetime values, it is sometimes expressed by a pick-off process ( $\lambda_{po}$ ) only. However, it can be reduced due to the additional decay constants related to *ortho-para* conversion ( $\lambda_{conv}$ ), for example, and intrinsic decay of a triplet state  $\lambda_T$ . The respective total decay constants can be described by the following relationships:

$$(2) \quad \begin{aligned} \lambda_3 &= \lambda_{po} + \lambda_T \approx \lambda_{po} && \text{without O}_2 \\ \lambda_3 &= \lambda_{po} + \lambda_{conv} + \lambda_T = \lambda_{po} + \lambda_{conv} && \text{in presence of O}_2 \end{aligned}$$

where

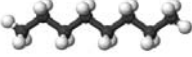



$$(3) \quad \lambda_{conv} = x \cdot K_{conv}$$

It is expected that the value of  $\lambda_{conv}$  will depend not only on the solubility of oxygen  $x$  [6], and the conversion constant  $K_{conv}$ , but also on the temperature  $T$ .

It is generally accepted that the *ortho-para* conversion plays an important role in liquid phase only. It turns out, however, that in some compounds the penetration (dissolving) of oxygen takes place even when the sample is not in liquid form, but a few degrees prior to melting [7].

Several organic materials were selected to study the *ortho-para* conversion in the liquid phase and the solubility of oxygen in the rigid phase. They are representative of the organic compounds composed of carbon and hydrogen atoms: *n*-alkanes, alcohols, branched isomer of alkane, cycloalkane. Selected compounds are structurally different (due to the arrangement of their atoms in the molecule), have different physical properties (e.g. melting points, a type of occurring rigid phase) and chemical properties (e.g. reactivity), but because the conversion takes place by reaction of Ps with O<sub>2</sub> molecules, but not in the medium (like in pick-off process), it seems that the medium does not play any role.

**Table 1.** Selected properties of the investigated materials at 300 K

Name of the compound and molecular formula	Chemical structure	Purity [%]	Melting point [K]	$\lambda_{conv}$ at 300 K [ $\mu\text{s}^{-1}$ ]	$K_{conv}$ [ $\text{ns}^{-1}$ ]
<i>n</i> -octane C <sub>8</sub> H <sub>18</sub>		≤99.5	214	149(18)	60
1-hexanol C <sub>6</sub> H <sub>14</sub> O		≤99	227	32(1)	33
Isooctane C <sub>8</sub> H <sub>18</sub>		99.8	165	129(5)	–
Cyclohexane C <sub>6</sub> H <sub>12</sub>		99.5	277–279	110(4)	72

## Experimental

The measurements in a broad range of temperatures above the melting point were performed for *n*-alkanes (*n*-octane, *n*-undecane, *n*-tridecane), alcohols (1-hexanol, 1-undecanol), branched isomer of alkane (isooctane), and cycloalkane (cyclohexane) (all from Sigma Aldrich). Some of them are briefly characterized in Table 1. Some PALS results for cyclohexane (at lower temperature) can be found in our previous paper [7].

The PAL spectra were measured using a standard fast-slow spectrometer with full width of half maximum (FWHM) better than 260 ps. The positron source <sup>22</sup>Na with activity 0.8 MBq in a Kapton envelope allowed 10<sup>6</sup> coincidences per hour statistics to be reached. All samples at room temperature were liquid and in such a form were placed in the measuring chamber. Measurements were conducted as a function of temperature in two regimes:

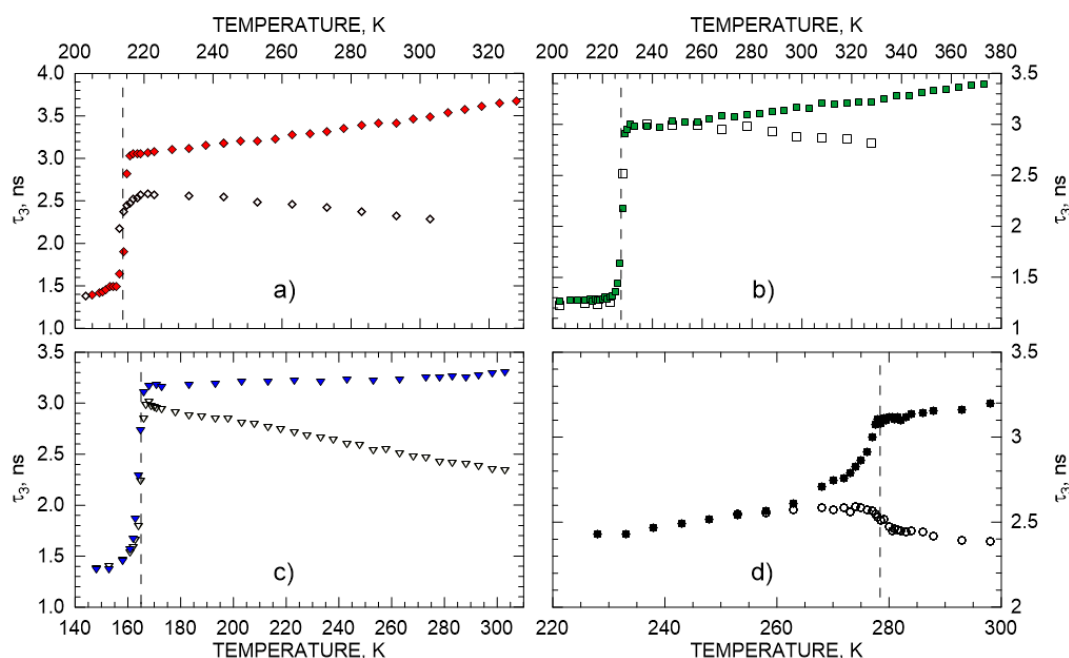
- in the presence of oxygen under normal pressure of the air, and
- in the vacuum chamber (without oxygen).

In the second case, it was necessary to prepare the sample for measurement by freeze-thaw technique – the removal of dissolved oxygen. The liquid sample enclosed in the chamber was cooled to 20 K below the melting point, then, after 10 min, the pumping gas accumulated above the solidified sample was started until a pressure of about 0.1 Pa was reached. Then the sample was melted and the cycle was repeated twice before the final measurement started.

The spectra were processed by LT 9.2 program [8]. Three exponential components ascribed to *p*-Ps decay, annihilation of free positrons, and *o*-Ps decay convoluted with the instrumental resolution curve were assumed. The correction for positron absorption in the Kapton envelope was also applied ( $I_s = 10\%$  and  $\tau_s = 374$  ps).

## Results and discussion

In our previous papers [9, 10] where samples were studied in vacuum, it was found that the *o*-Ps life-



**Fig. 1.** The *o*-Ps lifetime as a function of temperature in *n*-octane (a), 1-hexanol (b), isooctane (c), and cyclohexane (d) with and without air – empty and full symbols, respectively. Dashed lines denote the melting points.

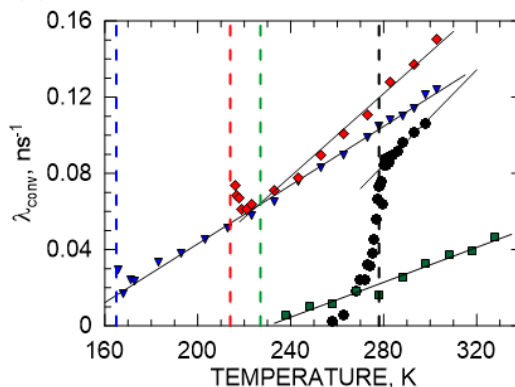
times shown as a function of the distance from the melting point ( $T - T_m$ ) in a homologous series of compounds (*n*-alkanes, alcohols) are arranged along one curve. The fact that the *o*-Ps lifetime does not depend on the carbon chain length (e.g. for *n*-alkanes with  $6 < n < 60$ ) allows for drawing a general conclusion on the basis of a single sample being a representative of the entire group of similar compounds. The compounds mentioned in the text above were selected as a test group; the measurements were performed as a function of temperature in vacuum and in air. The results for the four exemplary compounds are shown in Fig. 1. The presence of oxygen does not change the temperature of a phase transition point (melting point).

The tendency of  $\tau_3(T)$  changes in all compounds is the same: growth with the temperature – if a sample is devoid of paramagnetic molecules; decrease – if a sample is in contact with air. The divergence, that is the way of drawing apart of these two  $\tau_3(T)$  changes, can be attributed to processes associated with the interaction of positronium with oxygen molecules, among which the *ortho-para* conversion seems to be dominant.

In order to determine the rate  $\lambda_{\text{conv}}$  associated with the conversion of *ortho-para* one can use formula (2). As shown in Fig. 2, the  $\lambda_{\text{conv}}$  are different for different compounds but the trends of a change (slope vs.  $T$ ) in the alkanes and cyclohexane are very similar, while in the case of isooctane it differs slightly. A significant difference of  $\tau_3$  value for a sample with and without oxygen is observed in these three compounds in the melting point. In one of the investigated materials (alcohol) there is no noticeable difference between the sample containing oxygen and in the absence of its molecules up to 5 K above the melting point. At higher temperatures, the influence of O<sub>2</sub> is much smaller than in other cases. As can be seen from Fig. 2, three of  $\lambda_{\text{conv}}$  values are

arranged near  $130 \mu\text{s}^{-1}$ , at about 300 K, while for 1-hexanol, the value of  $\lambda_{\text{conv}}$  is more than four times smaller (see also Table 1).

The solubility of oxygen in many liquids has been reported in the work by Battino *et al.* [6]. In *n*-alkanes the mole fraction of gas  $x$  in the solution (the solubility mole fraction is defined in [6]) is a weak function of temperature; for the short chain alkanes, it increases slightly, while for the long chain ones, decreases slightly. For example, in *n*-octane,  $x = 21.28 \times 10^{-4}$  at 283 K, and decreases by approx. 0.7% when the temperature increases by 30 K. In cyclohexane, the solubility mole fraction increases vs.  $T$ , but in this solvent the values of  $x$  are lower than those in saturated hydrocarbons (e.g. at 283 K,  $x = 12.27 \times 10^{-4}$ ). The temperature dependence of solubility  $x$  in alcohols is not large – it decreases as the temperature rises (in 1-hexanol  $x \approx 9.7 \times 10^{-4}$  at 298 K). Assuming the solubility and relative  $\lambda_{\text{conv}}$ , one can estimate  $K_{\text{conv}}$  from Eq. (3) – determined values for respective com-



**Fig. 2.** The rate constant of *ortho-para* conversion  $\lambda_{\text{conv}}$  as a function of temperature. Diamonds – *n*-octane; dots – cyclohexane; triangles – isooctane; squares – 1-hexanol; dashed lines – melting points; solid lines – straight line fitted to the experimental points.

pounds are presented in Table 1. Changes of solubility are small and do not show any consistent trends in the compounds studied. However, the lifetime changes are similar for all organic compounds investigated. Presumably, oxygen solubility marginally changes  $\lambda_{\text{conv}}$ .

Compared to the other investigated substances, some uniqueness appeared herein in alcohol, in which structure an oxygen atom is built-in. The *o*-Ps lifetime value is the same in melting point for both cases regardless of the presence of oxygen (similar effect was observed in 1-undecanol, not presented here).

Taking into account the consideration presented above and the results from Fig. 1, one can also draw a conclusion that oxygen penetrates the medium before it melts. In three compounds a meaningful difference exists between two measurements: in absence and in presence of oxygen. It was earlier observed [7] that the presence of oxygen significantly modifies the *o*-Ps lifetime in the solid phase of cyclohexane. It can exist in the plastic phase prior to melting, and the easily visible effect of shortening the  $\tau_3$  value 15 K below the melting point is related to the presence of paramagnetic molecules. Two other compounds (*n*-octane and isooctane) have two phases: solid and liquid. And the increase of  $\tau_3$  is observed exactly at the phase transition point but lifetime reaches a lower value when the sample is in contact with air in comparison to  $\tau_3$  in vacuum. Probably the efficiency of oxygen penetration into the sample depends on its state, and in favorable conditions (e.g. increased plasticity of the sample), occurs also below the melting point.

## Conclusions

The presented study of the influence of paramagnetic oxygen molecules presence on *o*-Ps lifetime values is a quantitative and qualitative analysis of the phenomenon of *ortho-para* conversion. Based on the given small changes in oxygen solubility as a function of temperature, we can conclude that oxygen solubility does not affect significantly the  $\lambda_{\text{conv}}$  value. The variations of amount of dissolved oxygen are so small that the shortening of *o*-Ps lifetime cannot be

attributed to the increasing number of paramagnetic molecules with which Ps can interact. The efficiency of oxygen penetration into the sample can depend on its state and probably occurs also below the melting point.

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