Dissolved oxygen and positronium atom in liquid media

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Abstract. The interaction of positronium (Ps) with molecular oxygen dissolved in liquids (isooctane, cyclohexane, isopropanol and water) is experimentally investigated. For variation of the O₂ concentration the liquids were bubbled with Ar, air and O₂. For interpretation of the lifetime annihilation spectra a simple deconvolution of the spectra into three exponentials decaying in time was used. These exponents correspond to para-positronium, free positron and ortho-positronium annihilations. The total reaction rate constant of the Ps atom with dissolved oxygen (which is the sum of two - ortho-para-conversion (Ps → ¼ p-Ps + ¾ o-Ps) and oxidation (Ps + O₂ → e⁺ + O₂⁻) reaction rate constants) is obtained for each liquid.

Keywords: positron, annihilation, oxidation, ortho-para conversion, O₂, track processes

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1. INTRODUCTION
Positron annihilation spectroscopy (PAS) has numerous applications in material science such as studies of structural defects, free volume, porosity of materials. At the same time PAS is also applied to study radiolytic processes in chemistry, radiobiology and medicine [1]. In experiments with radiisotope positron sources, positrons are born and injected into the studied material with rather high energy. During ionization the slowing down positrons form tracks (clusters of ion-electron pairs along their trajectory), and after getting thermalized e⁺ start to explore the surrounding medium. Because typical lifetimes of the positron states (0.1-10 ns) are of the order of characteristic times of the intratrack processes in molecular media, the positron turns out to be a convenient probe for radiation phenomena.

In nonconducting substances, a thermalized e⁺ easily forms Ps, which is a bound state of e⁺ and e⁻ (the lightest analog of a hydrogen atom). The formation of Ps occurs in the final part of the e⁺ track (the positron blob) as a result of the combination of a thermalized positron with one of the track electrons. Depending on the relative orientation of e⁺ and e⁻ spins, the Ps atom can exist either in the para-state (p-Ps) with
a spin equal to zero, or in the ortho-state (o-Ps) with a spin equal to 1 [2].

In most molecular liquids, the o-Ps lifetime is much shorter than it is in vacuo (142 ns). It is decreased to a few ns, because of the so-called pick-off process, when the positron (in Ps) undergoes $2\gamma$-annihilation with one of the nearest molecular electrons, whose spin is anti-parallel to the positron's spin. Nevertheless, the o-Ps atom can take part in chemical reactions not only with intratrack radiolytic products (in water, these are hydrated electrons, $\text{H}_3\text{O}^+$, $\text{OH}^-$-radicals), but also with dissolved substances, for example, with molecular oxygen, $\text{O}_2$ [3].

Having a magnetic moment, an adjacent-to-Ps $\text{O}_2$ molecule is able to initiate the process of Ps ortho-para-conversion of Ps (o-Ps $\rightarrow$ p-Ps $\rightarrow 2\gamma$), which leads to a reduction in the observed o-Ps lifetime. In addition, the Ps oxidation is also possible, Ps $+ \text{O}_2 \rightarrow e^+ + \text{O}_2^-$, which shortens the o-Ps lifetime as well. To distinguish between these two reactions is very difficult.

In this work, we present the results of PAS experiments in organic liquids (isooctane, cyclohexane, isopropanol) and in water. Our aim is to determine the reaction rate constants (oxidation and conversion) of the Ps atom with dissolved oxygen.

Recently, an interest to shortening of the Ps lifetime (quenching) when its interacts with dissolved $\text{O}_2$ has increased in connection with the so-called "oxygen effect", known in radiobiology. It turns out that an excess of oxygen leads to removing of a cancer tumor because of reactions involving the active forms of $\text{O}_2$. Lack of oxygen protects healthy tissues. However, it is not so easy to take an advantage of this circumstance during radiotherapy: if we saturate blood with oxygen, it does not enter the tumor cells, since there are few blood tubes and capillaries in the tumor. Cancer cells are adopted to survive in conditions of lacking of oxygen. That is why they are radioresistant. Nevertheless, this effect is important when testing healthy and cancerous tissues of living organisms by the methods of positron annihilation spectroscopy [4].

2. EXPERIMENT

All the reagents used were purchased from Russian Chemist (www.rushim.ru). Unlike previous studies [5, 6] we did not use the freeze-thaw method to remove dissolved $\text{O}_2$ to avoid the risk of damaging the positron source during freezing and evacuation. Therefore, oxygen was removed from the liquid phase by its bubbling with chemically pure argon. For determination of the rate constants of the Ps $+ \text{O}_2$ reactions, the liquids were bubbled either with air or pure oxygen to increase the $\text{O}_2$ concentration. The gases were previously cleaned by means of blowing them through dry alkali KOH and then through nanosieves Metrohm 0.3 nm previously kept for 24 h in forvacuum at 250°C. Next, the purified gas was fed into a hermetically sealed vial containing the studied liquid. Input/output of the gas was performed by means of two long medical needles, tightly inserted into the lid of the vial.

The positron source was made from a 10 mm diameter, 0.2 mm thick titanium washer. Its central part (6 mm diameter) was welded on both sides with 10 μm titanium foils. In-between them a radioactive powder of $\text{TiCl}_4$, containing
about 7.5 MBq of $^{44}$Ti, was deposited. The positron source was fixed in the center of the vial using stainless steel clip. The clip itself was tightly fixed in the lid of the vial. The source correction was determined in a series of separate measurements of the reference (pure, well-annealed) samples (Al, Si, Fe and W). From these measurements we concluded that for the present experiments with liquids the source correction is 13%. It consists of the following components $I_1 = 32\%$, $t_1 = 0.15$ ns; $I_2 = 50\%$, $t_2 = 0.38$ ns; $I_3 = 18\%$ and $t_3 = 1.8$ ns.

The lifetime annihilation spectra were recorded using two $\gamma$-detectors with BaF$_2$ scintillators and fast timing nanosecond electronic units from ORTEC. The time resolution of the annihilation spectrometer was 280 ps. Spectra were recorded sequentially for each hour during one day. The total number of "start-stop" coincidence in each spectrum was about 1 million. All measurements were done at 20°C. The obtained spectra were deconvoluted into 3 exponentials with the help of LT-10 software [9].

3. ORTHO-PARA CONVERSION AND OXIDATION OF PS IN THE PRESENCE OF DISSOLVED O$_2$

Immediately after its birth, as a result of radioactive transformations of $^{44}$Ti-$^{44}$Sc-$^{44}$Ca radioactive nuclei, the positron has a rather large kinetic energy (about 1 MeV). Within the next 10 ps, it loses its energy down to thermal energy because of ionization slowing down. At the end of its track in molecular media, the thermalized positron can combine with one of the electrons knocked out through ionization along the track. This process results in the formation of the quasi-free positronium, which transforms into a localized state (Ps bubble state) within 50-100 ps. The conventional approach to interpretation of the positron lifetime spectra does not consider such short times. In this case differential equations describing these processes are as follows:

\[
\frac{\dot{n}_p(t)}{4} = -\frac{\lambda_{\text{pp}}}{4} n_p(t), \quad n_p(0) = \frac{P_{\text{ps}}}{4} \quad (1)
\]
\[
\frac{\dot{n}_s(t)}{4} = -\frac{\lambda_{\text{ps}}}{4} n_s(t) + \frac{\lambda_{\text{ps}}}{4} n_p(t), \quad n_s(0) = 1 - n_p(t) \quad (2)
\]
\[
\frac{\dot{n}_o(t)}{4} = -\frac{\lambda_{\text{ps}}}{4} n_o(t), \quad \lambda_o = \lambda_{\text{ps}} + \frac{\lambda_{\text{pp}}}{4} + \frac{\lambda_{\text{ox}}}{4}, \quad n_o(0) = \frac{3P_{\text{ps}}}{4} \quad (3)
\]

Here, $n_p(t)$, $n_s(t)$ and $n_o(t)$ are probabilities of observing the thermalized solvated positron and the Ps atom localized in a bubble in ortho- and para-state, respectively; $\lambda_{\text{ps}}$ is the pick-off annihilation rate constant of Ps and $\lambda_{\text{ox}} = k_{\text{ox}} c_{O_2}^{(t)}$ and $\lambda_{\text{pp}} = k_{\text{pp}} c_{O_2}^{(t)}$ are the oxidation and ortho-para conversion rate constants. $c_{O_2}^{(t)}$ being the concentration of molecular oxygen. $\lambda_{\gamma} \approx 8 \text{ ns}^{-1}$ is the $2\gamma$-annihilation of p-Ps. In the above equations we neglected the para-to-ortho process, since, due to the rather low O$_2$ concentrations used, this reaction appears kinetically negligible as compared to the fast $2\gamma$-decay of p-Ps. Solving Eqs. (1-3) gives the following

\[
n_p(t) = (1 - P_{\text{ps}}) e^{-\lambda_o t} + \frac{3P_{\text{ps}}}{4} \frac{\lambda_o}{\lambda_p - \lambda_o} (e^{-\lambda_p t} - e^{-\lambda_o t}) \quad (4)
\]
\[
n_p(t) = \frac{P_{\text{ps}}}{4} e^{-\lambda_o t} + \frac{3P_{\text{ps}}}{4} \frac{\lambda_{\text{pp}} / 4}{\lambda_p - \lambda_o} (e^{-\lambda_p t} - e^{-\lambda_o t}) \quad (5)
\]
\[
n_o(t) = \frac{3P_{\text{ps}}}{4} e^{-\lambda_o t}, \quad \lambda_o = \lambda_{\text{ps}} + \frac{\lambda_{\text{pp}}}{4} + \lambda_{\text{ox}} \quad (6)
\]

As a result, it turns out that the lifetime annihilation spectrum consists of three exponentials.
Usually, for a formal description of the LT spectra, the quantities \( I_1, I_2, I_3, \tau_1, \tau_2 \) and \( \tau_3 \) are considered as free adjustable parameters. A typical form of temporary annihilation spectra is shown in Fig. 1.

In Table 1 we have shown the results of such a formal 3-exponential treatment of the LT spectra measured in cyclohexane, isooctane, isopropanol and water before and after bubbling argon, oxygen and air through these liquids. The obtained \( e^+ \) and o-Ps lifetimes are in agreement with the results of previous measurements [5, 6] done with deaerated liquids.

**Table 1.** Parameters of the 3-exponential decomposition of the LT spectra of the initially aerated isooctane, cyclohexane, isopropanol and water, and also after their bubbling with argon, oxygen and air at room temperature.

| Liquid         | \( I_1, \% \) | \( \tau_1, \text{ps} \) | \( I_2, \% \) | \( \tau_2, \text{ns} \) | \( I_3, \% \) | \( \tau_3, \text{ns} \) | \( \lambda_0 = 1/\tau_0, \text{ns}^{-1} \) |
|----------------|--------------|----------------|--------------|----------------|--------------|----------------|----------------|
| Isooctane      |              |                |              |                |              |                |                |
| Ar bubbling    | 24.6         | 148(1)         | 32.3(1)      | 0.45(1)        | 43.1(1)      | 4.01(1)        | 0.249(3)       |
| air bubbling   | 21.8         | 145(1)         | 34.2(4)      | 0.45(1)        | 43.8(1)      | 2.51(1)        | 0.398(5)       |
| before bubbling| 22.6         | 149(1)         | 32.7(1)      | 0.46(1)        | 44.7(1)      | 2.546(3)       | 0.393(2)       |
| O\(_2\) bubbling| 14           | 116(3)         | 31(1)        | 0.43(1)        | 55(2)        | 1.077(6)       | 0.929(2)       |
|                |              |                |              |                |              |                |                |
| Cyclohexane    |              |                |              |                |              |                |                |
| Ar bubbling    | 25           | 165(2)         | 38.9(4)      | 0.44(1)        | 36.1(4)      | 3.26(4)        | 0.307(12)      |
| air bubbling   | 23.9         | 165(2)         | 40.1(4)      | 0.45(1)        | 36.1(4)      | 2.515(40)      | 0.398(16)      |
| O\(_2\) bubbling| 17.4         | 141(2)         | 44.3(4)      | 0.43(1)        | 38.4(4)      | 1.42(4)        | 0.703(29)      |
|                |              |                |              |                |              |                |                |
| Isopropanol    |              |                |              |                |              |                |                |
| Ar bubbling    | 21.7         | 194(3)         | 56(1)        | 0.44(2)        | 22.5(1)      | 3.75(10)       | 0.267(26)      |
| air bubbling   | 21           | 193(3)         | 56(1)        | 0.44(2)        | 22.5(10)     | 3.2(1)         | 0.313(30)      |
| Продувка O\(_2\) | 16           | 173(4)         | 61(1)        | 0.43(2)        | 22.9(8)      | 1.905(10)      | 0.525(6)       |
|                |              |                |              |                |              |                |                |
| Water          |              |                |              |                |              |                |                |
| Ar bubbling    | 31           | 213(4)         | 44(4)        | 0.44(2)        | 25(4)        | 1.833(16)      | 0.546(9)       |
| air bubbling   | 25           | 194(3)         | 49(1)        | 0.42(2)        | 25.5(1)      | 1.802(15)      | 0.555(9)       |
| O\(_2\) bubbling| 7            | 200(3)         | 47(4)        | 0.42(1)        | 26(3)        | 1.746(14)      | 0.573(8)       |
4. CONCENTRATIONS OF DISSOLVED O2 IN THE STUDIED LIQUIDS

Gas solubility is often expressed by the Ostwald coefficient, \( L \), which is the ratio of the gas concentration in the gas phase to its concentration in the liquid: \( L = c^{(G)}_{O_2} / c^{(L)}_{O_2} \) (in some papers, the Ostwald coefficient is defined as \( c^{(G)}_{O_2} / c^{(L)}_{O_2} \)). Gas solubility may also be expressed in terms of the mole fraction, \( x \), which is the ratio of the number of moles of the solute (gas molecules) to the total number of moles of all substances per unit volume of the solution.

When pure oxygen is bubbled through a liquid, its partial pressure is 1 atm and its gas phase concentration is \( c^{(G)}_{O_2} \approx 1/24.1 \) mole/liter, since at 20°C 1 mole of an ideal gas occupies 24.1 liters. The concentrations of O\(_2\) in liquids can be easily obtained, knowing values of the Ostwald coefficients (Table 2): \( L = c^{(L)}_{O_2} / c^{(G)}_{O_2} \). When air is blown through a liquid, the \( O_2 \) concentration in the gas phase is 0.21 times less: \( c^{(G)}_{O_2} = 0.0087 \) mole/liter (since partial \( O_2 \) pressure in air is 0.21 atm). The \( O_2 \) concentration in the liquid phase decreases in the same proportion.

In our experiments dissolved oxygen is completely removed from a liquid phase after 2 hours bubbling of argon through the liquid.

5. DETERMINATION OF THE TOTAL PS-O\(_2\) REACTION RATE CONSTANTS

If we neglect any influence of the intratrack radiolytic products on Ps (which can also promote Ps oxidation and conversion, although mostly on a short time-scale) and in the absence of dissolved oxygen, the \( o-Ps \) lifetime is determined only by the pick-off annihilation of \( e^+ \) with one of the electrons of nearby molecules. In the presence of \( O_2 \), the \( o-Ps \) lifetime can also be shortened because of conversion to the para-state and Ps oxidation:

\[
\lambda_o(c^{(L)}_{O_2}) = \lambda_{po} + \frac{\lambda_{opc}}{4} + \lambda_{ox} = \lambda_{po} + k_{Ps+O_2} \cdot c^{(L)}_{O_2},
\]

where

\[
k_{Ps+O_2} = \frac{k_{opc}}{4} + \lambda_{ox}.
\]

Our experimental data for \( \lambda_o(c^{(L)}_{O_2}) \) at different \( O_2 \) concentrations in liquids are summarized in Tables 1 and 2. Approximating these dependencies using Eq. 8, one can determine the values of the "total" rate constant \( k_{Ps+O_2} \) reaction with oxygen and the pick-off annihilation rate \( \lambda_{po} \) (see Table 2 and Fig. 2).

| Liquid          | \( c^{(L)}_{O_2} / c^{(G)}_{O_2} \) | \( c^{(L)}_{O_2} - M \) | \( c^{(G)}_{O_2} = 0.0415 \) M | \( c^{(L)}_{O_2} - M \) | \( c^{(G)}_{O_2} = 0.0415 \) M | \( k_{Ps+O_2} \), \( M^{-1} s^{-1} \) | \( \lambda_{po} \), 1/ns |
|----------------|---------------------------------|--------------------------|--------------------------------|--------------------------|--------------------------------|--------------------------------|--------------------------|
| Isooctane      | 0.362 [10]                      | 0.0148                   | 3.2·10^{-3}                    | 4.50(6)·10^{-10}         | 0.25(1)                        |                               |                          |
|                | 0.3725 [11]                     | 0.0154                   |                                |                          |                                |                               |                          |
| Cyclohexane    | 0.27 [10, 12]                   | 0.0112                   | 2.35·10^{-3}                   | 3.51(7)·10^{-10}         | 0.31(1)                        |                               |                          |
| Isopropanol    | 0.2463 [11]                     | 0.010                    | 2.1·10^{-3}                    | 2.61(6)·10^{-10}         | 0.26(1)                        |                               |                          |
| Water          | 0.0334 [10]                     | 0.00139                  | 2.9·10^{-4}                    | 1.86(10)·10^{-10}        | 0.55(2)                        |                               |                          |
In Fig. 3 our data for $k_{ps+o_2}$ are plotted vs. the inverse dynamic viscosity $1/\eta$ of the liquids. Similar data were published in [13]. Linear dependence of $k_{ps+o_2}$ over $T/\eta$ indicates that the Ps + O$_2$ reaction is diffusion-controlled:

\[
k_{ps+o_2} = 4\pi(D_{ps} + D_{o_2})(R_{ps} + R_{o_2}),
\]

\[
D_{ps} + D_{o_2} = \frac{k_B T}{4\pi \eta R_{ps}} + \frac{k_B T}{6\pi \eta R_{o_2}} \propto \frac{T}{\eta}.
\] (9)

Here $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $D_{ps}$ and $D_{o_2}$ are the diffusion coefficients of the reactants, $R_{ps} \approx 3$-4 Å and $R_{o_2} \approx 2$Å are bubble radii of Ps and O$_2$.

Eq. 9 brings us two problems. The first one is that the rate constant should tend to zero with increasing viscosity of the solvent, whereas Fig. 3 shows that it is not ($k_{ps+o_2}$ remains finite at high viscosity). This means that the interaction of Ps and O$_2$ occurs not only at a distance of a direct contact of the reactants, but also at greater distances (for example, electron or Ps as a whole may tunnel to the oxygen molecule) [14]. The second problem is that the predicted value of the slope of the dependence $k_{ps+o_2}$ versus $1/\eta$ according to Eq. (9) is several times smaller than it really is in Fig. 3. It may indicate that we must distinguish between reaction radii of the reagents and their “hydrodynamic” radii entering the diffusion coefficients. Seemingly, the reaction radii are larger then the hydrodynamic ones.

Based only on the concentration dependence of the quenching rate $\lambda_o(e_{o_2}^{(l)})$, it is impossible to distinguish the mechanisms of interaction between Ps and O$_2$ (conversion and oxidation). Therefore, it is impossible to understand which of these processes dominates. This requires more detailed analysis of the entire form of annihilation spectra, but not just their long-lived tail.

6. CONCLUSION

The interaction of the Ps atom with oxygen dissolved in liquid media is a rather complex problem. In fact it is a special case of a general
problem of random walks of a particle and its acceptors when they can interact on a random distance [15]. The problem is even more complex because formation of Ps atoms in nano-bubbles does not happen at the same moment of time (say, $t = 0$). Instead every formation event happens to have a certain random time delay. These delays occur due to existence of a delocalized intermediate transient state of an $e^+ - e^-$ pair named quasi-free positronium.

When processing the lifetime positron spectra, we used their traditional decomposition into three decreasing exponents. In fact, the total rate constant characterizing the interaction of Ps with $O_2$ was determined by analyzing the slope of the long-lived component of the lifetime spectrum, i.e., by changing the ortho-Ps annihilation rate with varying concentration of dissolved oxygen in the studied liquids.

The obtained results show that in organic media the influence of dissolved oxygen on the behavior of the positronium atom is very significant, which is associated with the high solubility of molecular oxygen in these liquids. In contrast, the oxygen effect in water is small (due to low solubility of $O_2$) and weekly affect the parameters of annihilation spectra. Therefore, pure water is often used as a “reference” medium for checking the operation of positron spectrometers.

The presence of oxygen, apparently, has no effect on the lifetime of “free” positrons. This lifetime is determined by the structure of solvated positron (in polar media), i.e. the configuration of molecules that directly contact the positron, and with difference of the average electron density in these solvents (the number of electrons per unit volume).

REFERENCES
1. Duplatre G, Billard I. Organic and Inorganic Chemistry of the Positron and Positronium. In: Principles and Applications of Positron & Positronium Chemistry. Eds. Jean YC, Mallon PE, Schrader DM. World Scientific, Singapore-Hong Kong, 2003.
2. Positron and Positronium Chemistry. Eds. Schrader DM, Jean YC. In: Studies in physical and theoretical chemistry. Elsevier, Amsterdam-New York, 1988.
3. Consolati G, Genco I, Pegoraro M, Zanderighi L. Positron annihilation lifetime (PAL) in poly[1-(trimethylsilyl)propine] (PTMSP): Free volume determination and time dependence of permeability. J. Polym. Sci. B Polym. Phys., 1996, 34(2):357-367, doi: 10.1002/(SICI)1099-0488(19960130).
4. Jasinska B, Zgardzinska B, Cholubek G et al. Human Tissue Investigations Using PALS Technique -- Free Radicals Influence. Acta Physica Polonica A, 2017, 132(5):556-1558.
5. Kobayashi YJ. Chem. Soc. Faraday Trans., 1991, 87:3641.
6. Mogensen OE. Positron Annihilation in Chemistry. Springer Verlag, Berlin etc, 1995.
7. Zgardzinska B, Bialko W, Jasinska B. Ortho-para spin conversion of Ps by paramagnetic $O_2$ dissolved in organic compounds. Nukleonika, 2015, 60(4):801-804. DOI: 10.1515/nuka-2015-0144.
8. Karbowski A, Fedus K, Suzewski K, Bruzdowska J, Karwasz G. Acta Physica Polonica A, 2017, 132(5):1466, doi: 10.12693/APhysPolA.132.1466.
9. http://prac.us.edu.pl/~kansy/index.php?id=lt10.

10. Clever HL, Battino R, Miyamoto H, Yampolski Yu, Young CL. IUPAC-NIST Solubility Data Series. 103. Oxygen and Ozone in Water, Aqueous Solutions, and Organic Liquids (Supplement to Solubility Data Series Volume 7). *Journal of Physical and Chemical Reference Data*, 2014, 43:033102; doi: 10.1063/1.4883876.

11. Kretschmer CB, Nowakowska Ja, Wiebe R. Solubility of Oxygen and Nitrogen in Organic Solvents from -25 to 50 C. *Industrial and Engineering Chemistry*, 1946, 38(5):506-509.

12. Battino R, Rettich TR, Tominaga T. The Solubility of Oxygen and Ozone in Liquids. *Journal of Physical and Chemical Reference Data*, 1983, 12:163-178; doi: 10.1063/1.555680.

13. Lee J, Celitans GJ. Oxygen and Nitric Oxide Quenching of Positronium in Liquids. *Journal of Chemical Physics*, 1966, 44:2506; doi: 10.1063/1.1727072.

14. Byakov VM, Petukhov VR. J. Radioanal. Nucl. Chem. Letters, 1984, 85(1):67.

15. Stepanov SV, Byakov VM. To the Theory of Nonstationary Diffusion-Controlled Tunnelling Chemical Reactions. *Radiation Physics and Chemistry*, 2003, 68:643-646; doi:10.1016/S0969-806X(03)00284-6.