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Early processes in positron and positronium chemistry: possible scavenging of epithermal e^+ by nitrate ion in aqueous solutions

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Abstract. Positron ionization slowing down, formation of the positron track, reactions of e^+ with track species and its interaction with a scavenger on a subpicosecond timescale, including the process of the positronium formation process are discussed. Interpretation of the positron annihilation lifetime data on positronium formation in aqueous solutions of NO_3^- anions, known as efficient scavengers of the presolvated track electrons, suggests that these ions may also capture epithermal (presolvated) positrons as well.

1. Introduction

Positrons (e^+) as well as positronium atoms (Ps) are recognized as probes of the early radiolytic physicochemical processes. This is due to the fact that the formation of the positronium atom in molecular media takes place on a very short (picosecond) time scale through interaction of the thermalized positron with one of the electrons in the e^+ track [1]. Therefore, introducing electron scavengers into the medium can modify the Ps formation process in a controllable way.

Obviously, the informative potentiality of positron spectroscopy strongly depends on the reliability of a theory describing processes in the positron track, since it deciphers the information coded in the annihilation spectra. So, realistic models are needed for the e^+ track structure, e^+ ionization slowing down [2], thermalization and transformation of the released energy into heat [3, 4], intratrack reactions (ion-electron recombination, solvation, interaction with scavengers), Ps formation process and finally Ps interaction with chemically active radiolytic species [5].

The usual treatment of the measured annihilation spectra in the case of Positron Annihilation Lifetime Spectroscopy (PALS) is reduced to their deconvolution into a set of decaying time exponentials, or of Gaussians in the case of angular correlation of annihilation radiation and Doppler broadening of annihilation radiation. The outcome of such analyses of the spectra are the lifetimes/widths of these components and the corresponding intensities [6, 7].



However, realistic physicochemical processes within the fast positron track, especially in its terminal part (which is termed a blob), suggest some more complex behavior, particularly when different scavengers are dissolved in the studied medium, capable to react with epithermal (presolvated) particles (positrons and track electrons). The inhomogeneous spatial distribution of the track species and their outdiffusion become also an important factor: diffusion kinetics cannot be expressed in terms of mere exponentials or Gaussians [7].

In this case, the use of reaction rate constants (reaction radii or cross-sections), diffusion coefficients, initial size of the terminal positron blob and Ps contact density as the adjustable parameters is physically much more meaningful than the above mentioned “intensities” and lifetimes of some exponential functions. In the following, possible reactions of the presolvated e^+ and e^- with scavengers, taking as an example aqueous solutions of nitrate ions, are discussed.

2. Formation of the positron track

Positrons, produced in nuclear β^+ -decay, have initial energies of several hundreds of keV. Passing through a medium they lose energy via ionization. Within 5-10 ps the positron energy drops below the ionization threshold, Fig. 1.

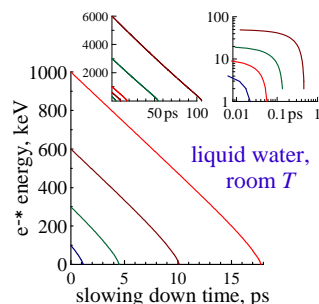


Figure 1. Typical times of ionization slowing down of e^+/e^- vs. its initial kinetic energy in liquid water at room temperature [physics.nist.gov/PhysRefData/Star/Text/ESTAR-u.html].

When the e^+ energy becomes less than the blob formation energy, W_{bl} ($\lesssim 0.5$ keV or so), the positron creates its terminal blob [1]. The diffusion motion of e^+ in the blob becomes more pronounced: the direction of its momentum changes frequently due to elastic scattering and ionization of surrounding molecules. Mostly all intrablob ionizations are confined within a sphere of radius a_{bl} . The terminal positron blob contains a few tens of ion-electron pairs: $n_0 \approx W_{bl}/W_{iep} \approx 30$, where the average energy W_{iep} required to produce one ion-electron pair is 16-20 eV. The formation of the terminal blob lasts less than 0.01 ps. Further approach towards thermal equilibrium (from about 10 eV down to thermal energies) proceeds primarily via excitations of intra- and intermolecular vibrations and usually takes a few tens of femtoseconds. The ultimate stage of transformation of the projectile positron as well as of secondary track electrons is solvation (in water – hydration). The electron hydration time is about 0.3 ps [8].

3. Reactions of hot electrons and positrons

During the slowing down process subionizing (hot, presolvated) electrons e^{-*} (or positron e^{+*}) can be captured by some solute molecules (or ions): $e^{-*} + S \rightarrow S^{-*}$. Subexcitation electrons cannot promote electronic transitions in host molecules, but may excite the solute molecules, this occurring at some definite energy W_* depending on the structure of the excited states S^{-*} , Fig. 2. Below, we shall consider electron trapping, but it may proceed with positrons also.

The fraction φ_e of electrons escaping the resonance capture by the solute (c_S is the solute concentration) depends on the energy spectrum of the subionizing electrons $f(W_0)$ and their stopping power due to excitation of vibrations [2]:

$$\varphi_e(c_S) = \int_0^\infty dW_0 f(W_0) \exp \left[-c_S \int_0^{W_0} \frac{\sigma(W)dW}{|dW/dx|_{vib}} \right]. \quad (1)$$

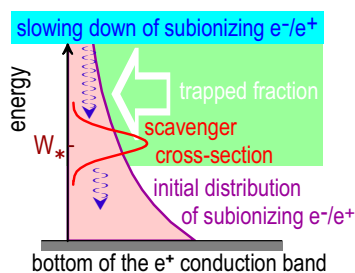


Figure 2. Resonance trapping of e^- or e^+ , having the energy $W \approx W_*$, by the scavenger S.

(the decrease in the scavenger concentration c_S inside the blob due to the reaction with hot electrons is neglected here. For simplicity we may assume that the capture cross-section $\sigma(W)$ is nonzero in a rather narrow energy range: $\sigma(W) \approx \sigma_0 \delta(W - W_*)$. Substituting this to Eq.1 we easily obtain:

$$\varphi_e(c_S) \approx 1 - F_- + F_- \cdot e^{-c_S/c_{37}^-}, \quad F_- = \int_{W_*}^{\infty} f(W_0) dW_0, \quad \frac{1}{c_{37}^-} = \frac{\sigma_0}{|dW/dx|_{vib}} \Big|_{W \approx W_*}. \quad (2)$$

Here $1 - F_-$ represents the fraction of track electrons escaping resonance capture even at large S concentration. These electrons are knocked out from molecules with energies below W_* and therefore do not interact with the scavenger.

In a similar way, the solute may also react with subionizing positrons. In this case $\varphi_p = 1 - F_+ + F_+ \exp(-c_S/c_{37}^+)$ would represent the fraction of positrons escaping a resonance capture by S. Fig. 3 illustrates effects of hot electron and positron scavenging.

If the capture cross-section of electrons (positrons) is located on the energy axis near the bottom of the conduction band ($1 - F_- \rightarrow 0$), the scavenger is able to capture almost all presolvated (quasifree) e^- (these electrons are precursors of the hydrated electrons). Such a situation is completed when nitrate ions are added into water. In this case the fraction φ_e of the track electrons ending up hydrated decreases exponentially with increasing c_S (the scavenger

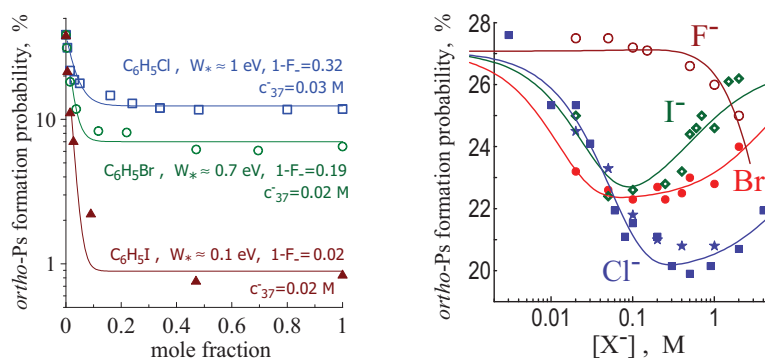


Figure 3. Left: Hot electron scavenging in benzene. Values of ortho-Ps formation probabilities are shown in benzene solutions of C_6H_5Cl (\square), C_6H_5Br (\circ) and C_6H_5I (\blacktriangle) [Anisimov O A, Molin Yu N Proc. 4th Int. Conf. Positron Annihilation, Helsingør, Danmark, G31, (1976)]. A correlation appears between the inhibition efficiency, F_- , and the energies W_* at which electron trapping by scavengers in a gas phase takes place. Solid lines are calculated according to Eq. 2. Right: Hot positron scavenging in aqueous solutions of alkali halide ions [Duplâtre G et al. 1978 Radiat. Phys. Chem. **11**, 199; Beling C D, Smith F A 1983 Chem.Phys. **81**, 243]. The increase of the Ps yield at higher c_S is due to reactions of halogen ions with H_2O^+ .

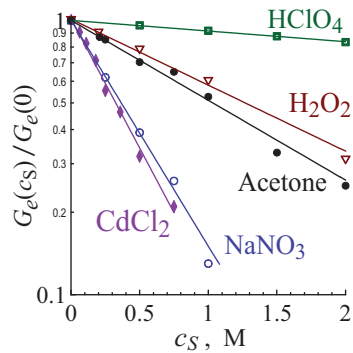
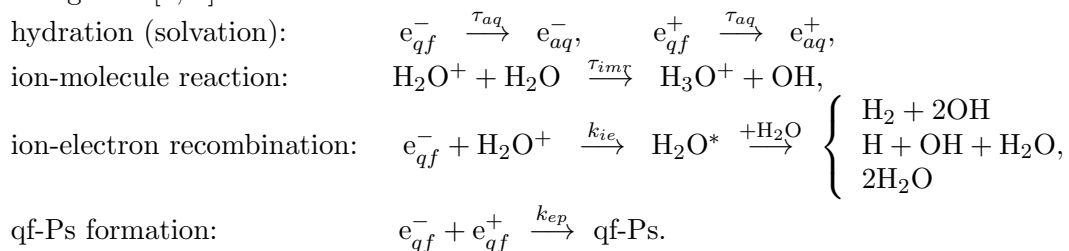


Figure 4. Exponential inhibition of the yield of the hydrated electron in aqueous solutions of various electron scavengers [Wolff R K, Bronskill M J, Hunt J W 1970 J. Chem. Phys. **53**(11), 4211].

concentration): $\varphi_e \approx \exp(-c_S/c_{\text{NO}_3^-})$. Therefore, in the same way, the yield of hydrated electrons is decreased: $G_e(c_S) \approx G_e(0) \exp(-c_S/c_{\text{NO}_3^-})$, where $c_{\text{NO}_3^-} = 0.53$ M and $G_e(0) \approx 4.3$ electrons per 100 eV is the e_{aq}^- yield in pure water, Fig. 4.

4. Reactions of thermalized quasi-free e^- and e^+ . Formation of e_{aq}^- , H_2 and qf-Ps

Now let us consider the next stage – the processes occurring in the e^+ blob with participation of quasi-free (thermalized, but not yet solvated) electrons e_{qf}^- , positrons e_{qf}^+ and primary radical-cations (holes, H_2O^+). As we have seen above, the scavenger S (nitrate ions NO_3^-) does not react with thermalized electrons, but with epithermal ones. The most important reactions at this stage are [2, 5]



Here $\tau_{aq} \approx 0.3$ ps is the hydration times of e_{qf}^- and e_{qf}^+ , assumed to be the same. τ_{imr} is the time of ion-molecule reaction. qf-Ps is the quasi-free positronium atom (precursor of the Ps bubble state), k_{ie} , k_{ep} are recombination reaction rate constants. This scheme assumes that Ps formation proceeds via the reaction of the thermalized positron with one of the track electrons, in competition with the other intratrack processes including hydration and recombination.

The above processes may be described by the following kinetic equations:

$$\frac{\partial c_j(\mathbf{r}, t)}{\partial t} = D_j \nabla^2 c_j - \sum_{i(\neq j)} k_{ij} c_i c_j - c_j / \tau_j, \quad c_j(\mathbf{r}, t = 0) \propto e^{-r^2/a_{bi}^2}, \quad j = \{i, e, p\}, \quad (3)$$

where c_i , c_e and c_p are the concentrations of H_2O^+ , e_{qf}^- and e_{qf}^+ , respectively, at a point \mathbf{r} measured from the blob center at time t measured from the end of thermalization. D_j is the corresponding diffusion coefficient and k_{ij} is the reaction rate constant.

For an approximate solution of Eqs. 3, one may use the prescribed diffusion method. It assumes that $c_j(\mathbf{r}, t) \approx n_j(t)G_j(\mathbf{r}, t, D_j)$, where G_j is the normalized Gaussian function (the Green function of the free diffusion equation) [2, 5]. Integrating Eqs. 3 over the whole volume, we obtain equations for the total numbers n_j of the species in the e^+ blob:

$$\dot{n}_i = -k_{ie}n_i n_e / V_{ie} - n_i / \tau_{imr}, \quad n_i(0) = n_0, \quad (4)$$

$$\dot{n}_e = -k_{ie}n_i n_e / V_{ie} - n_e / \tau_{aq}, \quad n_e(0) = n_0 \varphi_e, \quad (5)$$

$$\dot{n}_p = -k_{ep}n_e n_p/V_{ep} - n_p/\tau_{aq}, \quad n_p(0) = \varphi_p, \quad (6)$$

$$V_{ij} = V_0^{ij}(1 + t/\tau_{ij})^{3/2}, \quad V_0^{ij} = [\pi(a_i^2 + a_j^2)]^{3/2}, \quad \tau_{ij} = \frac{a_i^2 + a_j^2}{4(D_i + D_j)}.$$

Here $n_0 \approx 30-40$ is the initial number of ion-electron pairs in the blob. In accordance with the assumption of the ambipolar diffusion of the blob particles and electrical neutrality of the blob, we adopt that all $D_j \rightarrow D_{amb}$, $a_j \approx a_{bl}$ and $V_{ij} \approx V_0(1 + t/\tau)^{3/2}$, where $V_0 = (2\pi a_{bl}^2)^{3/2}$ and $\tau = a_{bl}^2/4D_{amb}$ is a characteristic time of the blob expansion. In water, thermalized e^- , e^+ and H_2O^+ disappear much faster than the blob expands. Therefore this expansion may be neglected: $V_{ij}(t) \approx V_0$.

To calculate the observable formation probabilities of e_{aq}^- , H_2 and qf-Ps, we have to perform the following integrations:

$$P_{H_2O^*} = \int_0^\infty \frac{k_{ie}n_i n_e dt}{n_0 V_0}, \quad P_{e_{aq}} = \int_0^\infty \frac{n_e dt}{n_0 \tau_{aq}}, \quad P_{qf-Ps} = \int_0^\infty \frac{k_{ep}n_e n_p dt}{V_0}. \quad (7)$$

Here, we adopt that excited water molecules give molecular hydrogen in approximately one third of all cases. To calculate these integrals we assume that H_2O^+ , e_{qf}^- and e_{qf}^+ disappear in time exponentially ($\propto e^{-w_j t}$) with the corresponding decay rates

$$w_i \approx \tau_{imr}^{-1}, \quad w_e \approx w_p \approx \tau_{aq}^{-1}, \quad (8)$$

which will be obtained later, using balance equations. Substituting these exponents into Eqs. 7, we easily obtain

$$P_{H_2O^*} = \frac{\varphi_e w_{ie}}{w_e + w_i}, \quad P_{e_{aq}} = \frac{\varphi_e}{\tau_{aq} w_e} = \frac{G_e(c_S)}{G_{H_2O}}, \quad P_{qf-Ps} = \frac{\varphi_e \varphi_p w_{ep}}{w_e + w_p}, \quad (9)$$

where $w_{ie} = k_{ie}n_0/V_0$ and $w_{ep} = k_{ep}n_0/V_0$ are the corresponding recombination rate constants (ion-electron and electron-positron) and G_{H_2O} is the yield of decomposition of water (= 6.3 molecules per 100 eV) [9]. Now let us take into account the conservation laws for electrons, ions and the positron:

$$\varphi_e = P_{H_2O^*} + P_{e_{aq}}, \quad 1 = P_{H_2O^*} + \frac{1}{w_i \tau_{imr}}, \quad \varphi_p = P_{qf-Ps} + \frac{\varphi_p}{w_p \tau_{aq}}. \quad (10)$$

Substituting the expressions for $P_{H_2O^*}$, $P_{e_{aq}}$ and P_{qf-Ps} to these three equations, we can deduce three unknown quantities w_e , w_i and w_p , solving simple quadratic equations.

To reduce the number of uncertain parameters, we assume that 1) $w_{imr} = 1/\tau_{aq}$; 2) from the experimental values of the e_{aq}^- yield in pure water $G_e(0)/G_{H_2O} \approx 4.3/6.3$ using Eqs. 9 one can find that $w_{ie} \approx 0.625/\tau_{aq}$; 3) from the probability of formation of a quasi-free positronium $P_{qf-Ps} = 0.46-0.48$ (roughly it is the sum $I_1 + I_3$ of intensities of the shortlived and longlived components of the LT spectrum) at room temperature we obtain $w_{ep} \approx 1.6/\tau_{aq}$.

Note that the further intratrack reactions (qf-Ps transformation into a bubble state, Ps oxidation reactions with chemically active track species (OH, H_3O^+), Ps ortho-para conversion) must be considered by solving the diffusion-recombination equations which describe processes on the nanosecond time scale [5, 7].

5. Results and discussion

Fig. 5 shows how the qf-Ps formation probability in $NaNO_3$ aqueous solutions changes with the concentration of NO_3^- ions at 17 and 39 °C. It is seen that simple extrapolation

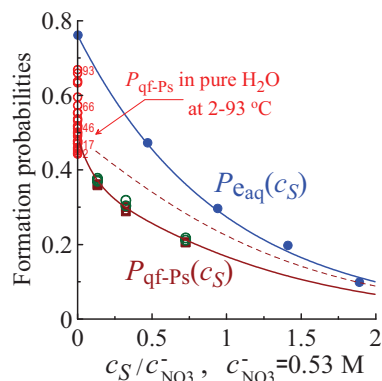


Figure 5. Formation probabilities of e_{aq}^- in NO_3^- aqueous solutions at room T (data are recalculated from Fig. 4) and of qf-Ps at nearly room temperatures (\circ – 21 °C, \square – 39 °C [7]). In pure water $P_{\text{qf-Ps}}$ values are shown for a wider T range (2–93 °C). Solid lines are plotted according to Eqs. 9. It was used that $w_{ie}\tau_{aq} = 0.625$, $w_{imr}\tau_{aq} = 1$, $w_{ep}\tau_{aq} = 1.6$, $\varphi_e \approx \exp(-c_S/c_{\text{NO}_3}^-)$, where $c_{\text{NO}_3}^- = 0.53$ M and $\varphi_p = 1 - F_+ + F_+ \exp(-c_S/c_{\text{NO}_3}^+)$, where $F_+ = 0.25$ and $c_{\text{NO}_3}^+ = 0.06$ M. Dashed line shows inhibition of qf-Ps formation in case of absence of the trapping of presolvated positrons by NO_3^- ions, i.e. when $\varphi_p = 0$.

($\propto \exp(-c_S/c_{\text{NO}_3}^-)$) of these data (at non-zero c_S) to zero concentration (at $c_S = 0$) leads to a mismatch with $P_{\text{qf-Ps}}(0)$ values in pure water at the same temperatures. This discrepancy even increases at $T = 60$ –90 °C [7]. The dashed line in Fig. 5 shows the theoretically expected dependence for $P_{\text{qf-Ps}}(c_S)$ when trapping of hot positrons by NO_3^- is absent, i.e. if in Eq. 9 we put $\varphi_p = 0$. It is seen that the difference between the dashed and solid red curves is not small. It indicates that nitrate anions capture hot (epithermal) positrons to some extent.

It is also known that the NO_3^- ions react with the hydrated electrons (the rate constant is about $k(\text{NO}_3^-) \approx 10^{10} \text{ M}^{-1}\text{s}^{-1}$). Therefore, in a solution at concentration about 0.1 M, the NO_3^- ions capture most of the hydrated electrons in the e^+ blob during 1 ns: $1 - \exp[-k(\text{NO}_3^-) \cdot [\text{NO}_3^-] \cdot (1 \text{ ns})] \approx 2/3$ (the typical concentration of hydrated electrons therein is about 0.01 M). However, treatment of the AMOC and LT spectra in pure water and nitrate aqueous solutions has shown that Ps inhibition is well described by the theory, neglecting Ps formation as a result of combination of e_{aq}^- and the positron. Capture of the hydrated electrons by NO_3^- ions (which definitely takes place in the e^+ blob) does not affect the qf-Ps formation probability [7]. It follows that the hydrated e^- is not a Ps precursor, and the hydrated positron does not react with e_{aq}^- . Most likely, this is due to the low mobility of the hydrated species and to the minute energy gain in this reaction: the energy of the Ps bubble is only slightly below the sum of the energies of the hydrated e^+ and e^- , whereas significant rearrangement of the surrounding molecules is needed in the reaction. Anyway, further experimental investigations are (especially AMOC measurements) are very welcome in this direction.

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