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ON THE MECHANISM OF MUONIUM FORMATION IN LIQUID WATER

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Abstract—The experimental data on the influence of some solutes in water on formation probabilities of muonium, positronium and radiolytic hydrogen are compared. It is shown that the inhibiting action is very similar in all cases. This means that the formation mechanisms of muonium, positronium and radiolytic hydrogen have common features. Taking into account that the formation of radiolytic hydrogen and that of positronium proceeds via recombination mechanism with unsolvated electron as one of precursors, it is asserted that the muonium formation mechanism is similar.

It is usually believed that formation of a muonium atom arising during the slow down process of fast μ^+-muon in a medium proceeds via extraction of an electron from one of the surrounding molecules.[1] The muon kinetic energy at which the electron capture is the more probable is equal to the first ionization potential multiplied by the ratio of the muon mass to that of the electron. This corresponds to $\simeq 2$ keV. The analogous mechanism was suggested in its time for positronium formation during the slow down of positrons (see, for example, Ref. 2). In the last few years, however, arguments were forwarded in favour of positronium atom formation in a condensed medium via recombination of positron with one of the electrons expelled from the medium:[3-5]

$$e^+ + e^- \longrightarrow Ps. \qquad (1)$$
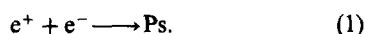
The recombination proceeds at the end part of the positron track when the positron kinetic energy becomes lower than $\simeq 1$ keV. In this energy region the positron transport length (the mean distance passed by the positron before its 90° scattering) is less than the mean distance between ionization acts, so that its movement takes a diffusion character and the space distribution of ions and electrons in the first approximation is spherically symmetrical around the thermalized positron centre. Therefore, at the end part of the positron track the conditions favouring for reactions (1) are formed as well as for the electron-ion recombination:

$$M^+ + e^- \longrightarrow Prod.$$
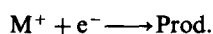
The latter takes place in the track of any ionizing particle. In water, for instance, the electron-ion recombination leads to formation of molecular hydrogen and of the most part of "primary" atomic hydrogen:[4,6]

$$H_2O^+ + e^- \overset{k}{\longrightarrow} \begin{array}{c} H_2 + Prod \\ H + Prod. \end{array} \qquad (2)$$
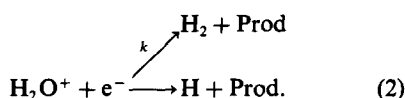
The common features of the Ps and radiolytic hydrogen formation via intratrack reactions (1) and (2) is revealed, particularly, in a similar influence of dissolved water substances, S, electron acceptors, on Ps and H_2 formation probabilities. Reacting with electrons these substances prevent H_2 and Ps formation:

$$S + e^- \overset{k_S}{\longrightarrow} S^-. \qquad (3)$$
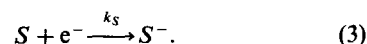
It appears that for a substance dissolved in water, the more the Ps formation is inhibited, the higher is its ability to inhibit the radiolytic hydrogen formation and the higher is its rate constant with unsolvated electron.[4,5]

Thus, it can be concluded that positronium and radiolytic hydrogen are formed by recombination reactions (1) and (2), respectively, with unsolvated electron as a common precursor.

The similar character of interaction with matter and that of movement of e^+ and μ^+ during their slowdown process allows one to assume that muonium formation proceeds via recombination

$$\mu^+ + e^- \longrightarrow Mu \qquad (4)$$
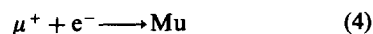
or at least that this reaction is an important source of muonium. The arguments in favour of Mu atom formation via reaction (4) were originally forwarded by Percival.[7] Contradictory responses in the literature justify the further analysis of this problem.

In this note an attempt is made to determine the recombination mechanism of muonium formation on the basis of available experimental data on formation probabilities, W, of positronium, muonium and radiolytic hydrogen in water when solutes are present, as was done earlier[4,6] for positronium and radiolytic hydrogen. For positronium this probability is measured directly: $W(Ps) = 4I_2/3$, where I_2 is the intensity of the long-lived *ortho*-positronium component. As a measure of muonium formation
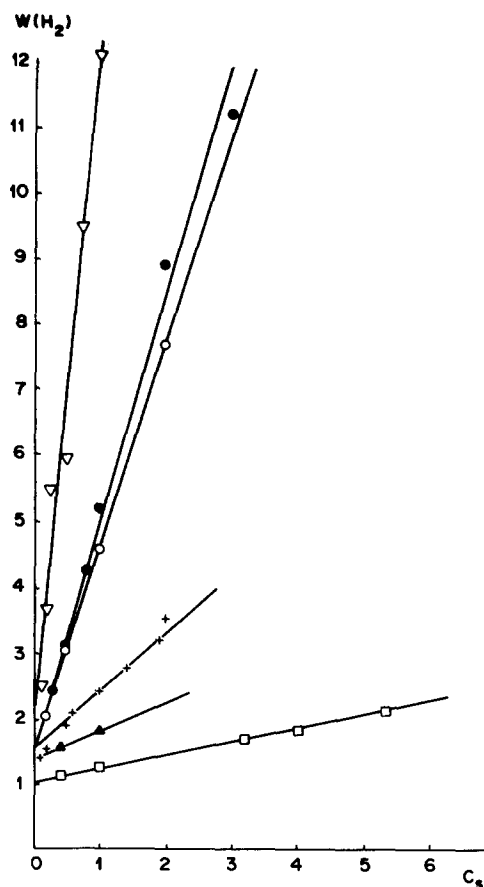
Fig. 1. Linear dependences of reciprocal yields of radiolytic hydrogen on concentrations of solutes in water: □, HClO₄[8]; ▲, CuSO₄[9]; +, H₂O₂[10]; ●, O, NO₃⁻ [11,12]; ▽, Cu(NO₃)₂.[13] For convenience of comparison with other data concentrations of Cu(NO₃)₂ are doubled. $G^0_{H_2} = 0.46$ molecule/100 eV is the hydrogen yield extrapolated to zero solute concentration.
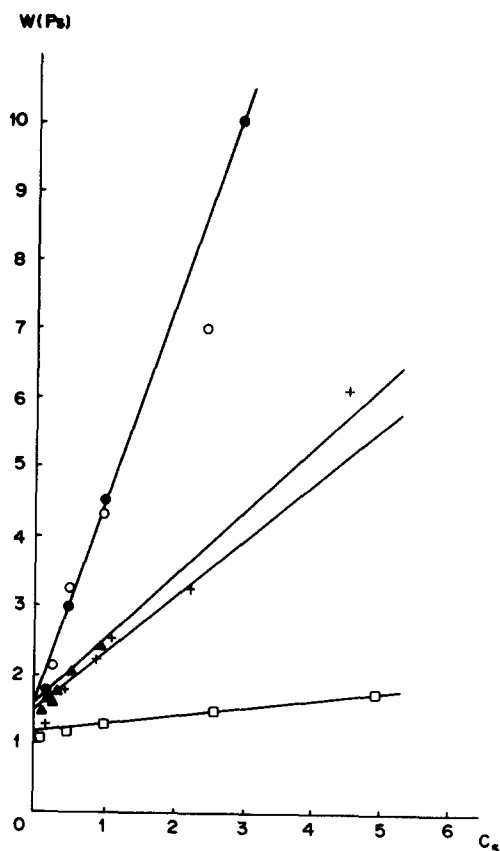
Fig. 2. Linear dependences of reciprocal positronium formation probabilities on concentration of solutes in water: □, HClO₄[14,15]; ▲, CuCl₂[16]; +, H₂O₂[17]; ●, O, HNO₃, KNO₃.[14]

molecules 100 eV is the full yield of water decomposition.

The experimental data on W for muonium, positronium and radiolytic hydrogen in aqueous solutions of various electron acceptors are presented in Figs 1–3. Their comparison shows that the probability dependences on the C_S, concentration of substances dissolved in water, are the same. Up to a reasonable accuracy these dependences can be approximated by eqn (5) derived from the recombination-diffusional model of radiolytic hydrogen and

probability one may use the value $[1 - P(\mu^+)]$, where $P(\mu^+)$ is the μ^+-muon polarization amplitude (it is assumed that the missing polarization is due to muonium atom reactions with paramagnetic particles, most probably, with electrons, in the muon track). For radiolytic hydrogen $W(H_2) = G_{H_2}/G_{-H_2O}$, where G_{H_2} is the molecular hydrogen formation yield in the process of water radiolysis and $G_{-H_2O} \simeq 6$

Table 1. Coefficients B_S for radiolytic hydrogen, positronium and muonium in various aqueous solutions

H₂	Cu(NO₃)₂	NO₃⁻	Cu²⁺	H₂O₂	ClO₄⁻
H₂	10.6	3.1–3.5	0.43–46ᵃ	0.9–1.1	0.18–0.20
Ps		2.8	0.5ᵇ	0.8	0.16
Mu	4.0	1.0–1.4	0.25 ± 0.05ᵃ	0.68 ± 0.03	0.08 ± 0.02
C_{37}^{-1}, M^{-1}	5.9ᶜ	2.4	1.1ᵈ	0.7	≤ 0.1
$10^{10} k(e_{aq} + S)$ $M^{-1}.s^{-1}$		1.8	1.5	1.2	≤ 10⁻⁵

ᵃDetermined in CuSO₄ solutions.
ᵇDetermined in CuCl₂ solutions.
ᶜCalculated as the sum of $C_{37}^{-1}(Cu^{2+})$ and $2 \cdot C_{37}^{-1}(NO_3^-)$.
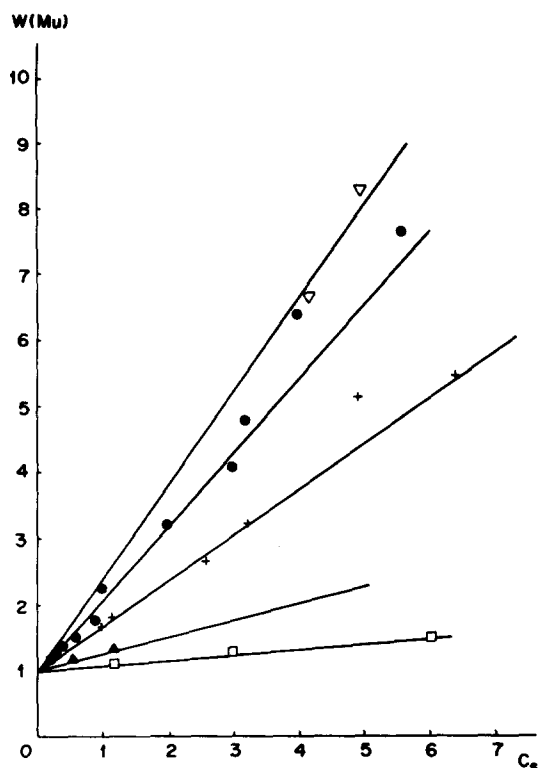ᵈDetermined in completely dissociated solutions of Cu(ClO₄)₂.[22]

Fig. 3. The dependences of $[1 - P(\mu^+)]^{-1}$ on concentration of solutes in water: $\square$, $HClO_4$[18]; $\blacktriangle$, $CuSO_4$[18]; $+$, H_2O_2[19]; $\bullet$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Zn(NO_3)_2$[18]; $\triangledown$, $Cu(NO_3)_2$.[18] For convenience of comparison with other data concentrations of $Mg(NO_3)_2$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, $Cu(NO_3)_2$ are doubled.

positronium formation; this equation is valid for C_S not too small:[20,17]

$$\frac{W_0}{W} = 1 + B_S C_S, \quad B_S = \frac{k_S}{k}\frac{V_0}{n_0}. \quad (5)$$

Here n_0 and V_0 are the initial number of electron–ion pairs in the diffusion part of the muon track and its volume, respectively. The values of coefficients B_S calculated from the data of Figs 1–3 are presented in Table 1. As may be seen, the abilities of solutes to inhibit muonium, positronium and radiolytic hydrogen formation are very similar. It is also seen that the inhibiting action activity of the mentioned substances does not correlate with their rate constants with respect to hydrated electron. On the contrary, the coefficients B_S correlate with C_{37}^{-1} values which

characterize the activity of substance S with respect to presolvated electron.[21] As the formation of positronium and radiolytic hydrogen in water proceeds via intratrack reactions (1) and (2), respectively, the above experimental data may be considered as an argument in favour of recombination mechanism of muonium formation in water.

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