

Effect of Added Water on the Radiolytic Hydrogen Yield and the Positronium Formation Probability in Liquid Dioxane

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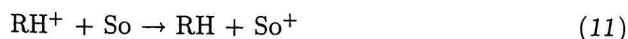
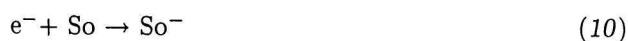
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ortho-Ps intensity measurements were made in dioxane—water mixtures (DWM) over wide concentration ranges, the purpose was to compare the changes in radiolytic hydrogen yield and o-Ps formation probability when dioxane is replaced by water. Water leads to a partial inhibiting of Ps formation and enhances the H₂ yield. The results point to the possibility of understanding H₂ and Ps formation in DWM on the basis of the previously formulated unified model for positronium and radiolytic hydrogen formation, if structure peculiarities of DWM are taken into account. The arguments are given that the influence of added water on the hydrogen formation in the radiolysis of DWM is not associated with the proton transfer from radical cations of dioxane to water molecules, but due to the capture of quasi-free electrons escaped the intratrack recombination with ions by water clusters took place in dioxane solutions of water.

This work adjoins our previous papers [1—4] concerning interrelations between early, subpicosecond processes in tracks of fast positrons and other ionizing particles, formed in the radiolysis of dielectric liquids and their mixtures.

As some other radiolytic products, Ps is formed *via* intratrack reactions (1, 2) between thermalized positron e⁺ and a secondary electron e⁻ in competition with other reactions (3—7) in the terminal, diffusion part of the positron track [1, 4]



Here e^{+**} (e^{-**}), e^{+*} (e^{-*}), e⁺ (e⁻), e_s⁺ (e_s⁻), denote fast, subionizing, thermalized quasi-free and solvated positron (electron), respectively. RH* is an electronically excited molecule. The Ps formation reaction (5) in the terminal blob of the positron track competes with the electron—ion recombination (reaction (6)) and with reactions (10—13) of electron, radical cations and positron scavenging by the surrounding molecules (solvent RH and solutes So) occurring in track of any ionizing particle, as well as with some other processes [3]. Therefore it turns out that Ps formation and early radiation chemistry processes are linked by common intratrack reactions.

In this paper we present positron annihilation data, which are important for understanding of radiation chemical processes in DWM [5, 6]. Our aim is to clarify the mechanism of the influence of added water on hydrogen formation in the radiolysis of DWM. We attempt to show that early radiation chemical reactions in DWM depend not only on the mixing ratio, but also on the molecular structure of the solution.

EXPERIMENTAL

The experimental procedures were essentially the same as previously described [2].

As usual, the observed positron lifetime spectra have been decomposed into three components. The short-lived components exhibiting lifetimes τ₁ and τ₂ and intensities I₁ and I₂ correspond to para-Ps and free e⁺ annihilations, respectively. The third or long-lived component with the lifetime τ₃ and intensity I₃ originated due to the ortho-Ps annihilations.

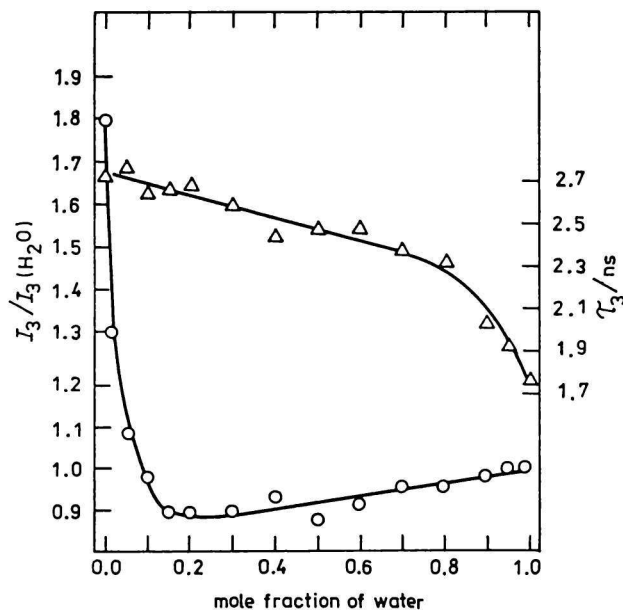


Fig. 1. Relative intensity $I_3/I_3(\text{H}_2\text{O})$ and lifetime τ_3 of ortho-Ps component in the dioxane—water mixture vs. mole fraction of water. Open circles (O) are experimental values of $I_3/I_3(\text{H}_2\text{O})$, solid line was calculated with the help of formula (26) using F , K_w , and β_w as adjustable parameters: $F = 0.58$, $K_w = 8 \text{ mol}^{-1} \text{ dm}^3$, $\beta_w = 0.1 \text{ mol}^{-1} \text{ dm}^3$. Triangles (Δ) are experimental values of τ_3 .

All the liquids were of good standard purity. They were used without further purification. Samples were degassed by use of the freeze-thaw method.

RESULTS AND DISCUSSION

The I_3 values of o-Ps formation probability, observed in DWM as a function of the mole fraction of water, φ_w , are shown in Fig. 1. From this figure it can be clearly seen that rather small additions of water (≈ 0.1 m.f.) drastically decrease I_3 to I_3^{min} value, which does not differ significantly from $I_3(\text{H}_2\text{O})$ value of the pure water.

The dependence of radiolytic hydrogen yield on the mole fraction φ_w of added light and heavy water is shown in Fig. 2 [5, 6]. An enhancement of $G(\text{H}_2)$ by H_2O is observed. As the water—dioxane composition is varied over the whole range $G(\text{H}_2)$ passes through a maximum. The same behaviour of $G(\text{HD})$ exists if in DWM H_2O is replaced by D_2O . The isotopic composition of the hydrogen yields for this case is also presented in Fig. 2. Both $G(\text{H}_2)$ and $G(\text{D}_2)$ change approximately linearly with the amount of added water in the range $\varphi_w \approx 0.0$ —1.0.

In the γ -irradiation of pure 1,4-dioxane $G(\text{H}_2)/(\text{molecule}/100 \text{ eV}) = 1.31$ was obtained [6]. Because $\{G(\text{H}_2)\}$ is suppressed down to ≈ 1.0 by the H-atom scavenger 1-hexane and by the electron scavengers, N_2O and $c\text{-C}_4\text{F}_8$, it was concluded that the yield

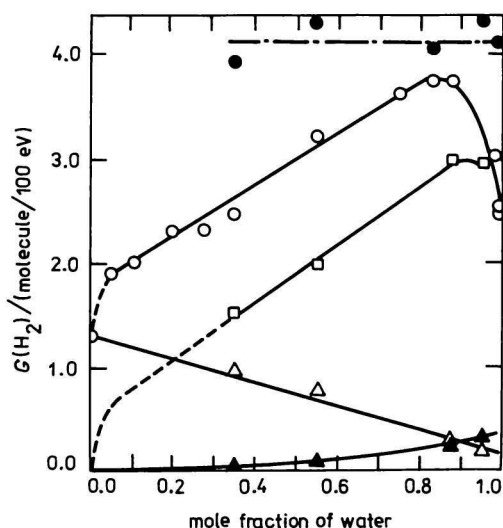
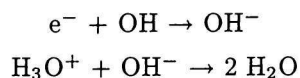


Fig. 2. Radiolytic hydrogen yield $G(\text{H}_2)$ in the dioxane—light water mixtures and partial hydrogen yields in dioxane—heavy water mixtures [6]. Open circles (O) and full circles (\bullet) correspond to binary dioxane—light water mixtures and to mixtures in the presence of $c(\frac{1}{2}\text{H}_2\text{SO}_4) = 0.1 \text{ mol dm}^{-3}$, respectively. Triangles and squares represent partial hydrogen yields in dioxane—heavy water mixtures: Δ $G(\text{H}_2)$; \square $G(\text{HD})$; \blacktriangle $G(\text{D}_2)$.

$\{G(\text{H}_2)\} \approx 0.3$ results from H atoms produced with $\approx 10\%$ efficiency in the neutralization of dioxane cations by electrons.

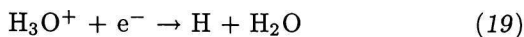
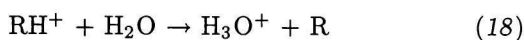
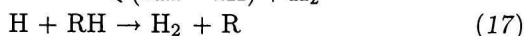
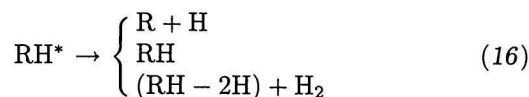
According to [5, 6], the major portion of the hydrogen yield obtained in γ -radiolysis of dioxane corresponding to $\{G(\text{H}_2)\} \approx 1.0$ is formed in a molecular elimination process, which does not have an electron precursor.

An enhancement of $G(\text{H}_2)$ by H_2O (and $G(\text{HD})$ by D_2O) was attributed to the proton transfer from a dioxane cation to give H_3O^+ , which on neutralization by an electron yields H atom with a unit efficiency. The observed maximum of $G(\text{H}_2)$ at $\varphi_w \approx 0.8$ —0.9 was related to a change of the yield of free solvated electrons vs. a change of dielectric properties of the medium. However, the more probable explanation seems to be the increased recombination due to increasing of the yield of OH radicals in water-rich region of φ_w



The following reactions were proposed in [5, 6] to describe the $G(\text{H}_2)$ dependence on the concentration of water in dioxane





Here RH stands for the dioxane molecule. In the reaction (14) the symbol e^- does not necessarily represent a particular degree of the electron.

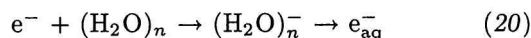
This scheme of the radiation-chemical processes in dioxane—water mixtures fails, however, in explanation of the behaviour of Ps formation probability *vs.* concentration of water (Fig. 1). The reaction (18) of dioxane radical cations with added water should enhance the Ps formation probability [3, 4], while actually the latter decreases.

The cause of this failure, according to our opinion, is quite obvious. The reaction scheme suggested in [5, 6] has been centred on the properties only of isolated molecules towards radiolytic products (e^- , RH^+ , *etc.*). However, structure effects in the liquid (hydrogen bonding, cluster formation) may have an important influence on the behaviour of some of these products.

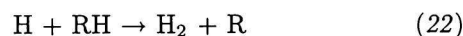
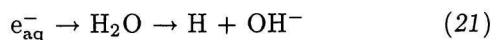
Basing on the above-mentioned identity of primary processes in tracks of positron and other ionizing particles [1, 3, 4] we suggest another mechanism for interaction of dioxane radiolytic products with water. This mechanism includes several additional processes and reactions of primary radiolytic products occurring due to the specific molecular structure of dioxane—water mixtures. In fact, hydrogen bonds between two molecules of water and dioxane are weaker than those of two water molecules [7]. Therefore, water molecules dissolved in nonpolar dioxane exist not only as monomers, but also as weakly hydrogen-bonded groups (associates or clusters). Thermodynamics of solutions and IR-spectroscopy data give evidence of the existence of such clusters. Water molecules are associated *via* hydrogen bonds into clusters also in pure water, not only in the solutions. It is known that dioxane enhances the association of free water molecules, *i.e.* it acts as a water-structure maker [8]. Alcohols form similar clusters in alkanes [9], and they may serve as traps of quasi-free electrons already at relatively low concentrations of the added alcohols [10, 11]. In fact, radiation-chemical studies indicate that electrons in diluted solutions of alcohols in alkanes and in pure alcohols have an identical absorption spectrum [10]. This phenomenon can be naturally explained by assuming that the dissolved molecules of alcohol form aggregates in these solutions, which are able to scavenge and solvate quasi-free electrons. Earlier we have

adopted the concept of electron trapping by alcohol clusters for explanation of our positron annihilation studies of alcohol solutions in hydrocarbons [2].

Water clusters in DWM could be characterized by V_0^{cl} , the ground state energy of quasi-free electrons, which is probably close to $V_0^{\text{w}} = -1.3$ eV of pure water, *i.e.* lower than V_0^{D} in pure dioxane. If this is true, these clusters may trap quasi-free electrons, e^- , according to reactions (20) and transform them into hydrated state



As the water content is increased, a greater fraction of the quasi-free electrons would be trapped. The electron, hydrated in a trap, is practically immobile and therefore only reacts with surrounding water molecules with formation of the H atom. The latter immediately picks up another H atom from a dioxane molecule



In contrast to reactions (17) and (19) suggested in [5, 6], reactions (20—22) are able to explain both the drastic enhancement of radiolytic hydrogen yield and the decrease of Ps formation probability when the mole fraction of water is ≤ 0.1 (Figs. 1 and 2).

At a rather small content of water ($0 < \varphi_{\text{w}} < 0.3$) the behaviour of I_3 may be interpreted with one of the empirical equations suggested by *Abbe et al.* [12] which was invoked to describe the process of a limited inhibition of Ps by a solute

$$I_3 = I_3^{\text{D}} \left(\frac{F}{1 + K_{\text{w}}c_{\text{w}}} + (1 - F) \right) \quad (23)$$

For adaptation of this formula to our case we have to interpret I_3^{D} as the intensity of o-Ps component in pure dioxane, c_{w} as the concentration of electron scavengers, that is of water clusters in dioxane; K_{w} and F are empirical parameters.

It has been demonstrated in [4] that eqn (23) follows from the unified diffusion recombination model of intratrack processes, which holds for quantitative description of positronium formation in dielectric liquids as well. In the frame of this model the empirical coefficients in eqn (23) acquire a clear physical meaning

$$K_{\text{w}} \approx \frac{1}{|dE/dx|_{E=E^*}} \int_{E^*}^{I_{\text{L}}} \sigma_{\text{s}}(E) dE \quad (24)$$

$$F = \int_{E^*}^{I_{\text{L}}} f(E) dE \quad (25)$$

Here σ_{s} is the electron capture cross-section by water clusters, $-dE/dx$ is the linear energy transfer

for subionizing electrons and $f(E)$ is the initial energy spectrum of electrons in the terminal blob of a positron track, normalized to unity: $\int_0^{E^L} f(E)dE = 1$.

From eqn (23) it follows that the electron capture by water clusters which we associate with the drastic decrease of I_3 at a low mole fraction of water should be considered as a threshold process, *i.e.* it should proceed only if the kinetic energy of slowing down electrons exceeds a threshold energy E^* . This is a necessary condition to get the observed (Fig. 1) limited inhibition of Ps formation by added water. Other arguments in favour of this view could be borrowed from the results of [13]. As shown in Fig. 1, a progressive increase of I_3 with the concentration of water added to dioxane occurs in the region $0.1 < \varphi_w < 1$. This small enhancement of I_3 by water we interpret in terms of a proton transfer reaction (18). The competition between reactions (10) and (11) reveals in an extreme dependence of I_3 as a function of mole fraction of water: I_3 drops initially to the value of about 23 % at 0.1 of water mole fraction, and subsequently slowly increases to 27 % in pure water. To take into account this effect we shall use for a quantitative description of I_3 *vs.* water mole fraction another, more complicated than eqn (23) formula derived in [4] (earlier similar formula was also empirically obtained by *Abbe et al.* [12])

$$I_3 = I_3^D \left(\frac{F}{1 + K_w c_w} + (1 - F) \right) \cdot \frac{1 + (I_3^w / I_3^{\min}) \cdot \beta_s c_s}{1 + \beta_s c_s} \quad (26)$$

Here

$$I_3^{\min} = I_3^D \cdot (1 - F) \quad (27)$$

$$I_3^w = \frac{2\tau(1 - F)}{\tau_{\text{ehr}}} \quad I_3^{\min} = \frac{2\tau(1 - F)}{\tau_{\text{ehr}}} \cdot (1 - \tau_h / \tau_{\text{ehr}})$$

$$\beta_s = k_s^h \cdot \tau_{\text{ehr}}$$

In calculations we assume that cluster concentration, c_w , linearly increases with increasing of total water concentration $[\text{H}_2\text{O}]$, as it takes place in hydrocarbon—alcohol mixtures [9]: $c_w = \gamma_w \cdot [\text{H}_2\text{O}]$, where γ_w is a dimensionless parameter. With this assumption eqn (26) describes well the experimental data in Fig. 1. The following values of parameters have been obtained: $F = 0.58$; $\gamma_w K_w \approx 5 \text{ mol}^{-1} \text{ dm}^3$; $\beta_s \approx 0.1 \text{ mol}^{-1} \text{ dm}^3$. If the decrease of I_3 when water is added to dioxane, is really due to quasi-free electron capture by water clusters and the constant K_w characterizes this process, it is natural to expect that K_w should not be essentially different from the similar value K_{al} for alcohol clusters in hydrocarbons. Our comparison of numerical values of K_w and K_{al} (determined from the data of [2]) shows that they are actually similar: $\gamma_{\text{al}} K_{\text{al}} \approx (3-5) \text{ mol}^{-1} \text{ dm}^3$. If $\gamma_w \approx \gamma_{\text{al}}$ and $\gamma_{\text{al}} \approx 0.6$ (see the insert in Fig. 3), one obtains $K_{\text{al}} \approx (5-8) \text{ mol}^{-1} \text{ dm}^3$, $K_w \approx 8 \text{ mol}^{-1} \text{ dm}^3$. The last value does not much differ from the quenching

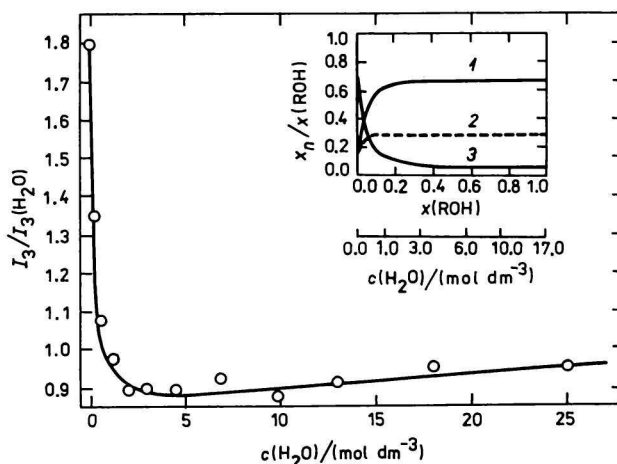


Fig. 3. Relative intensity of ortho-Ps component in the dioxane—water mixture $I_3/I_3(\text{H}_2\text{O})$ *vs.* the water concentration. Open circles (O) are experimental values of $I_3/I_3(\text{H}_2\text{O})$, solid line was calculated with the help of formula (26) using F, K_w , and β_w as adjustable parameters: $F = 0.58$, $K_w = 8 \text{ mol}^{-1} \text{ dm}^3$, $\beta_w = 0.1 \text{ mol}^{-1} \text{ dm}^3$. Insert: x_n — alcohol associates mole fraction, $x(\text{ROH})$ — alcohol mole fraction in hexane (1. polymer, 2. dimer, 3. monomer).

efficiency c_{37}^{-1} of the most effective solvated electron inhibitors. For instance, c_{37}^{-1} for CCl_4 and CHCl_3 in alcohols tends to $10 \text{ mol}^{-1} \text{ dm}^3$ [14].

From the relationship $\beta_s = k_s^h \cdot \tau_{\text{ehr}}$ it is possible to estimate the rate constant of the reaction of dioxane radical-cation k_s^h with water. Assuming that the order of magnitude of τ_{ier} is about 10^{-12} s , we obtain $k_s^h \equiv k(\text{RH}^+ + \text{H}_2\text{O}) \approx 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. This value agrees well with the rate constants of radical-cations with those solutes the ionization potentials of which differ from the ionization potentials of a solvent by the same quantity as acetone and dioxane.

CONCLUSION

Previously established analogy between the mechanism of Ps formation and intratrack radiation chemistry reactions allowed to give an unambiguous explanation for the radiolytic hydrogen formation process in the binary dioxane—water mixtures. We have demonstrated the role of positron annihilation experiments for the study of the mechanism of radiolysis in DMW and structure phenomena (cluster formation, hydrogen bonding, and *etc.*) in this system. The obtained results illustrate the importance of involving of positron annihilation data in the analysis of radiation-chemical reactions. Here we have obtained a single, but important example indicating how one can discriminate a dissolved substance (H_2O) according to its ability to react with electrons or holes of the solvent (dioxane).

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