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Primary Chemical Reactions Induced by Transformation of Radioactive Nuclei in Solids at Low Temperatures. Investigation by Means of the Emission Mössbauer and Positron Spectroscopies

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A set of early chemical reactions in grapes of ionization (blobs) arising in tracks of fast electrons and positrons in liquids as well as formed by the Auger electrons in frozen aqueous media around decaying Mössbauer ⁵⁷Co or ^{119m}Sn nuclei is suggested. The mechanism predicts a correlated variation of the formation probabilities of intrablob final products, namely Fe²⁺–Fe³⁺ or Sn²⁺–Sn⁴⁺ ions, positronium atom and molecular hydrogen with variation of temperature, degree of crystallinity, concentration of electron scavengers. These correlations indicate on similarity of chemical processes as in blobs created by ⁵⁷Co and ^{119m}Sn after their decay as well as in blobs produced in tracks of fast positrons and electrons.

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1. Introduction

We present a unified interpretation of chemical reactions in molecular solids, induced by fast e⁺ and e⁻ irradiation as well as by radioactive nuclear decay accompanied by emission of the Auger electrons and subsequent ionizations. Investigations of these processes are obviously interesting in view of understanding of physico-chemical transformations, taking place in media, containing radioactive

isotopes. It is also important for correct treatment of the data obtained by the Mössbauer spectroscopy, radiation chemistry and e^+ and Ps chemistry. Primarily we shall consider reactions in frozen aqueous solutions (77 K), nevertheless, our findings shed light on intratrack processes at normal conditions.

If an emission Mössbauer spectroscopy (EMS) is applied, a small amount of special (“Mössbauer”) isotopes (^{57}Co , $^{119\text{m}}\text{Sn}$) are added into investigated solid state system. A common property of these isotopes consists in production of the Auger ionization of the “daughter” atoms (^{57}Fe , ^{119}Sn), caused by E-capture or converted isomeric transition. These processes precede emission of the Mössbauer γ -quantum by ^{57}Fe or ^{119}Sn , which contains physico-chemical information about the daughter atoms and their environment [1].

Auger ionization converts the daughter atom into multi-charge ion (electric charge of ^{57}Fe ion could reach +8). This process is accompanied by emission of a large number of the Auger electrons with energies mainly above 10^2 eV. Together with X-rays within 10^{-14} s they produce ionization of many molecules in a spherical environment (of a nanometer scale) of the ion. In the literature on radiation chemistry such a cloud of tens or hundreds ion–electron pairs is called as blob [2, 3]. Here we shall call it as the Auger blob.

The blob is a structural element of the track of any ionizing particle. Usually it consists of 30–50 ion–electron pairs. It is created by a secondary electron with the energy 10^2 – 10^3 eV. A terminal part of the positron track is also the blob [3].

2. Chemical processes in blobs

Within $\approx 10^{-7}$ s after its birth ^{57}Fe nucleus emits a Mössbauer γ -quantum 14.4 keV, which is registered by a detector. It is important that the energy of the photon depends on the number of electrons, composing electronic shell of $^{57}\text{Fe}^{n+}$ ion, and, therefore, conveys information about n , at a time when it was emitted [1]. Initially electron affinity of $^{57}\text{Fe}^{n+}$ significantly exceeds first ionization potential of the surrounding molecules and neutralization of $^{57}\text{Fe}^{n+}$ proceeds by picking up electrons from them. By the time moment of emission of the Mössbauer photon the ion usually restores its electron shell up to one of its chemically stable states (Fe^{3+} or Fe^{2+}), mainly Fe^{3+} . We assume that reduction of Fe^{3+} to Fe^{2+} proceeds via recombination with quasi-free electrons, e^- , of the Auger blob



Reaction (1) is similar to the Ps formation in the positron blob



Therefore one may expect that in a given medium the formation probabilities of Fe^{2+} and Ps must be proportional to each other. Moreover, radiolytic hydrogen (H_2) in water is also a product of intrablob reaction (6) [3]. If so, the yields of Fe^{2+} , Ps and H_2 have to correlate in aqueous solutions. Reactions (1)–(2) have

to be supplemented with reactions, taking place in blobs of fast electrons, with participation of the radiolytic products of the medium. In frozen aqueous solutions the most important reactions are the following [2, 3]:

ionization of water molecules by the Auger electrons (e^{-**}):



thermalization of "hot" electrons (e^{-*}):



trapping of thermalized electrons (e^{-}) on structural traps with formation of trapped electrons (e_{tr}^{-}):



other chemical reactions:



3. Quantitative consequences of the model

From these reactions one may obtain quantitative relations concerning variation of the yields of *ortho*-Ps, $I_{o\text{-Ps}}$, radiolytic hydrogen, G_{H_2} , doubly charged Fe ion, $R(\text{Fe}^{2+})$, and hydrated electron, $G(e_{\text{aq}}^{-})$ vs. concentration c_{S} of electron scavenger (S). Inhibition of these yields may be approximated by the following expressions [3–5]:

$$I_{o\text{-Ps}} = I_{o\text{-Ps}}^0 / (1 + pc_{\text{S}}), \quad (13)$$

$$G_{\text{H}_2} = G_{\text{H}_2}^0 / (1 + hc_{\text{S}}), \quad (14)$$

$$R(\text{Fe}^{2+}) = R^0(\text{Fe}^{2+}) \exp(-fc_{\text{S}}), \quad (15)$$

$$G(e_{\text{aq}}^{-}) = G^0(e_{\text{aq}}^{-}) \exp(-qc_{\text{S}}). \quad (16)$$

Inhibition coefficients of *o*-Ps, H_2 , Fe^{2+} and e_{aq}^{-} (e_{tr}^{-}), namely p , h , f , and q characterize the reaction ability of S towards thermalized quasi-free electrons (e^{-}),

which we consider as the H_2 , $o\text{-Ps}$, Fe^{2+} and e_{aq}^- (e_{tr}^-) precursors. Each coefficient is proportional to the rate constant $k(e^- + \text{S})$ of quasi-free electron with S:

$$p \propto h \propto f \propto q \propto k(e^- + \text{S}). \quad (17)$$

Below we shall present experimental data, which prove consequences (13)–(16) of the model. Unfortunately, we have no possibility to compare data from different experiments in identical conditions. There are few radiation-chemical and positron annihilation data, obtained in frozen solutions, which can be directly confronted with data of emission Mössbauer spectroscopy. Nevertheless, correlations between the yields of the above mentioned species even under somewhat different conditions are meaningful and indicate on a similarity of the discussed processes in blobs.

4. Comparison with experiments

1. Using the data on the yield of Fe^{2+} (Fig. 1) in frozen aqueous solutions of NaClO_4 , H_2SO_4 , HClO_4 , and HNO_3 [6] at 77 K and Eq. (15), $R(\text{Fe}^{2+}) = \exp(-\sum_i f_i c_{\text{S}i})$, we obtained ratios of f_i for different ions, i.e. for electron scavengers existing in these solutions

$$f(\text{H}_3\text{O}^+) : f(\text{ClO}_4^-) : f(\text{NO}_3^-) \approx 0.04 : 0.05 : 0.1. \quad (18)$$

These ratios qualitatively agree with the ratios of coefficients q_i and p_i (see Eq. (13) and Eq. (16)), also characterizing reaction ability of the same ions towards quasi-free electron at room temperature [5, 7]:

$$q(\text{H}_3\text{O}^+) : q(\text{ClO}_4^-) : q(\text{NO}_3^-) \approx (\leq 0.1) : (\leq 0.1) : 2.4. \quad (19)$$

$$p(\text{H}_3\text{O}^+) : p(\text{ClO}_4^-) : p(\text{NO}_3^-) \approx (\leq 0.1) : 0.1 : 3.1. \quad (20)$$

The proximity of q and p in liquid water at room temperature and their partial deviation from values of f , found by means of EMS in frozen media are quite natural. What is important is that all ratios (18)–(20) differ significantly from the ratios

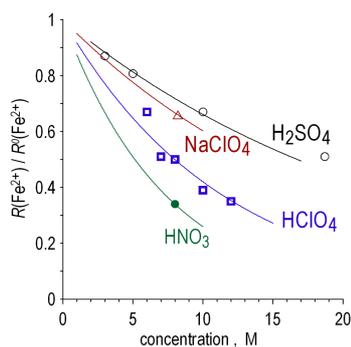


Fig. 1. Relative yields of Fe^{2+} in acid aqueous solutions frozen at 78 K. Solid lines (exponents) represent Eq. (15) [6].

of the reaction rate constants $k(e_{\text{aq}}^- + S_i)$ between S_i and hydrated electron [5]:

$$k(e_{\text{aq}}^- + \text{H}_3\text{O}^+) : k(e_{\text{aq}}^- + \text{ClO}_4^-) : k(e_{\text{aq}}^- + \text{NO}_3^-) = 1 : 0.1 : 1. \quad (21)$$

2. Figure 2 demonstrates similar inhibition efficiencies of G_{H_2} by Cr^{2+} and Cu^{2+} ions at room temperature, and similar action of these ions on the Sn^{2+} yield in frozen (77 K) aqueous solutions. This fact tells us about similar state and behavior of intrablob electrons in different types of blobs in spite of the large difference in temperature and phase state of the investigated samples.

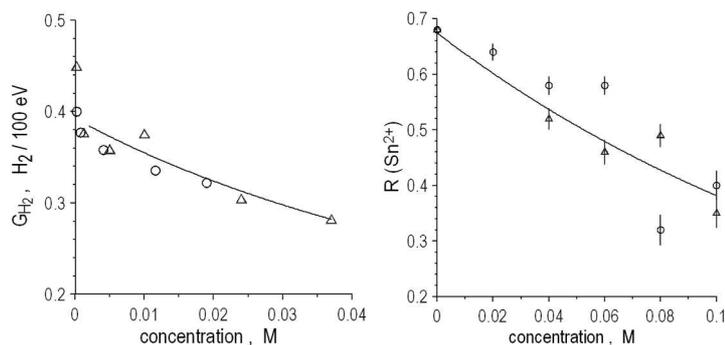


Fig. 2. On the left: dependence of radiolytic hydrogen yields vs. concentration of Cu^{2+} (\circ) and Cr^{2+} (Δ) ions in aqueous solutions at room temperature [7]. Solid line is an approximation by means of Eq. (14). On the right: dependence of the Sn^{2+} yield in frozen at 77 K solutions vs. concentration of salts CrCl_2 (Δ) and CuCl_2 (\circ) [8]. Sn^{2+} is the final product of ion–electron recombination of the $^{119\text{m}}\text{Sn}$ nucleus, after its converted isomer transition. Solid line is calculated with a help of Eq. (16).

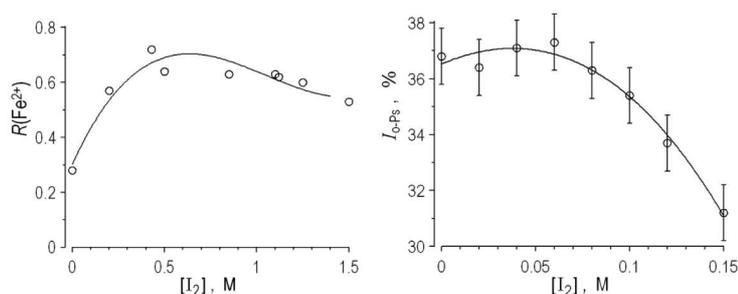


Fig. 3. On the left: Fe^{2+} yield in frozen at 77 K ethanol vs. I_2 concentration [9]. On the right: $o\text{-Ps}$ yield in liquid cyclohexane at room temperature vs. I_2 concentration [10]. Solid lines approximate the experimental data.

3. Figure 3 demonstrates complicate behavior of the Fe^{2+} yield (left) in frozen at 77 K glassy ethanol vs. concentration of I_2 . In liquid cyclohexane $o\text{-Ps}$ formation probability behaves similarly vs. concentration of I_2 (right).

4. Figure 4 shows correlation in variation of the yields of Fe^{2+} , H_2 , and Ps vs. temperature of the medium. All the yields increase with temperature. Temperature coefficients $\frac{1}{G_{\text{H}_2}} \frac{dG_{\text{H}_2}}{dT}$ and $\frac{1}{I_{o\text{Ps}}} \frac{dI_{o\text{Ps}}}{dT}$ are the same, but $\frac{1}{R(\text{Fe}^{2+})} \frac{dR(\text{Fe}^{2+})}{dT}$ is somewhat higher. Probably it is related with variation of the character of solvation of the ions.

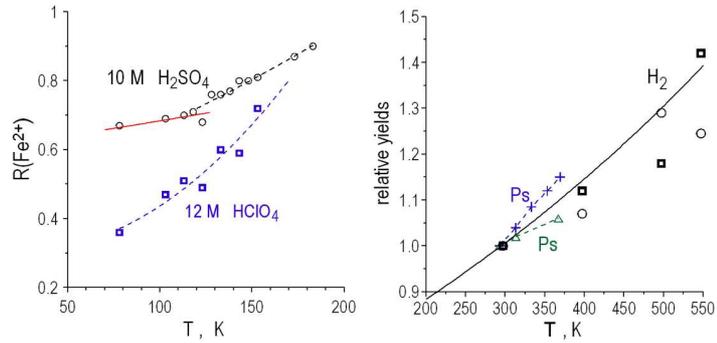


Fig. 4. On the left: temperature dependences of Fe^{2+} yields in frozen glassy solutions of 10 M H_2SO_4 (\circ) and 12 M HClO_4 (\square) [11]. On the right: relative Ps formation probability ($+$, Δ) in water and hydrogen yields under the action of fast neutrons (\square) and γ -rays (\circ) vs. temperature (see [12] and refs. therein). Solid lines are drawn with the temperature coefficients (see in text).

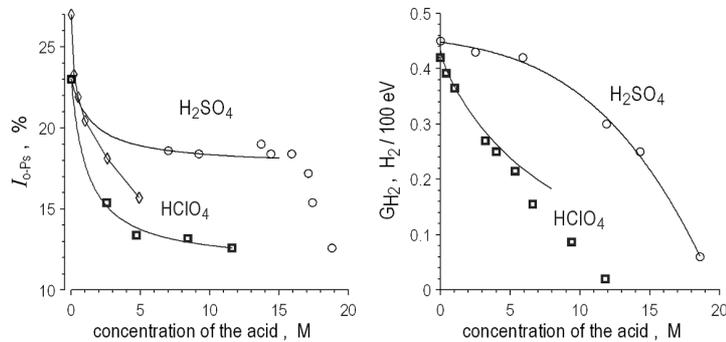


Fig. 5. On the left: o -Ps yields in concentrated solutions of H_2SO_4 (\circ — [13]) and HClO_4 (\square — [13]; \diamond — [14]). On the right: H_2 yields in concentrated solutions of H_2SO_4 (\circ — [15]) and HClO_4 (\square — [16]). Solid lines approximate the tendencies in variations of the data.

It is worth mentioning the difference of yields of Fe^{2+} in solutions of sulphuric and chloric acids, which are clearly seen at low temperatures. This difference holds for the yields of radiolytic hydrogen and o -Ps in solution of the same acids at room temperature (Fig. 5).

5. Conclusion

Similar character of an influence of concentration of dissolved substances, temperature and phase state on the yields of the Mössbauer ions $^{57}\text{Fe}^{2+}$, $^{119}\text{Sn}^{2+}$, $o\text{-Ps}$, radiolytic H_2 , and e_{S}^- is revealed. This fact supports our suggestion about similarity of early chemical reactions taking place in positron, electron, and Auger blobs.

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