

Primary Radiolytic Reactions in the Auger Blob Formed by Radioactive Transformation of ^{57}Co into ^{57}Fe in Frozen Aqueous Medium

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The emission of the Auger electrons during the formation of the Mössbauer nucleus ^{57}Fe leads not only to the formation of multicharged $^{57}\text{Fe}^{n+}$ ion, but also to the appearance of the Auger blob, a cloud of several hundreds of ion–electron pairs (H_2O^+ , e^-) in the solvent around the Fe ion. Fast radiation-chemical reactions therein determine the experimentally observable ratio of the yields of final chemically stable charged states of the Mössbauer ions (Fe^{3+} and Fe^{2+}). This ratio strongly depends on reaction rates constants between H_2O^+ , e^- , and the solute S. We have shown that in contrast to radiation chemical data the reactivity of NO_3^- anions with quasi-free track electrons in frozen aqueous solutions exceeds those of H_3O^+ , ClO_4^- , and HSO_4^- ions only by a factor of three instead of ≈ 100 which follows from the radiation chemical experiments.

DOI: [10.12693/APhysPolA.125.843](https://doi.org/10.12693/APhysPolA.125.843)

PACS: 76.80.+y, 82.50.Kx, 82.80.Ej

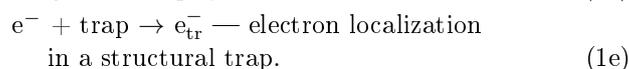
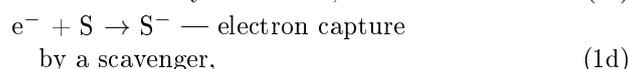
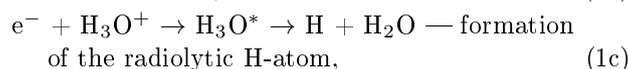
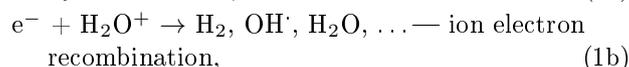
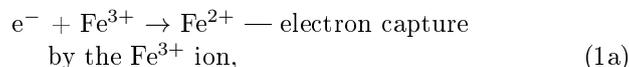
1. Introduction

Primary radiolytic processes turn out to be most difficult to investigate because of their rapidity and lack of suitable probes. In fact most of radiation-chemical information about intratrack radiolytic processes is obtained by the pulse radiolysis method and partly by EPR, photochemical methods and positron annihilation spectroscopy. As was shown in [1–3] emission Mössbauer spectroscopy (EMS) is also useful for investigating of early stages of radiolysis. The emission of the Auger electrons during the formation of the Mössbauer nucleus ^{57}Fe leads not only to the formation of multicharged $^{57}\text{Fe}^{n+}$ ion ($n \approx 4-8$), but also to the appearance of the Auger blob, a nanodimensional cloud of 200–300 ion–electron pairs (H_2O^+ , e^-) in the solvent around the Fe ion within 10^{-13} s. Further reactions in the Auger-blob (ion–electron recombination, electron localization, and scavenging) determine the experimentally observable ratio of the yields of the final chemically stable Mössbauer ions Fe^{3+} and Fe^{2+} . This ratio strongly depends on reactions between blob species (H_2O^+ , e^-) and the solute S. Usually the results obtained by different methods correlate with each other, although sometimes they may diverge. In this paper we have discussed such an example when the reactivity of NO_3^- anions with quasi-free track electrons in frozen aqueous solutions obtained by EMS [4, 5] differs by a factor of 30 from the results derived from the radiation chemical experiments [6, 7].

2. Theory

Reduction of Fe^{3+} ions into Fe^{2+} occurs because of trapping of the quasi-free blob electrons. Generally

speaking, intrablob reactions proceed together with out-diffusion of the blob species, but this out-diffusion is strongly hindered because of the low mobility of the positively charged ions in the disordered frozen medium (blob electrons are attracted to ions because of Coulombic interaction). This is the case of the so-called ambipolar diffusion expansion. The ambipolar out-diffusion is terminated by the localization of the quasi-free electrons on structural traps (it takes about 10^{-7} s). Thus the processes in the Auger blob may be summarized as follows:



Further behavior of the trapped electrons is governed by their tunneling to the positive ions or to the dissolved electron scavengers. However, this stage elapses over a much longer time.

The interaction between track electrons with different electron scavengers dissolved in water at room temperature has been studied quite well since the 1970s using the pulse-radiolysis method. Some acceptors, for example, Cd^{2+} and NO_3^- react effectively not only with thermalized quasi-free electrons, but also with hot (epithermal) electrons [6]. This phenomenon results in a typical exponential suppression of the yield of the hydrated electrons

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$$G_{\text{aq}}(c_S) \sim \exp(c_S/c_{37}), \quad (2)$$

where c_{37} is the concentration of the scavenger at which the yield of hydrated electrons decreases by $1/e$. For the NO_3^- ions, $c_{37} = 0.52$ M [6].

In contrast to the nitrate ions, such ions as H_3O^+ , ClO_4^- , and HSO_4^- react very weakly with quasi-free track electrons ($c_{37} \geq 10$ M) and mostly interact with the solvated electrons.

A similar result is observed at low temperatures [7]. The yield of atomic hydrogen was measured by means of the electron paramagnetic resonance (EPR) technique in aqueous 5 M solution of perchloric acid frozen at 77 K with NO_3^- ions added in concentrations of up to several mol/l. It was shown that the presence of NO_3^- ions at concentrations of ≈ 0.1 M, which is low in comparison to the concentration of H_3O^+ ions (5 M), results in a considerable decrease in the yield of atomic hydrogen. It is known that atomic hydrogen is formed due to the capture of track electrons by the H_3O^+ ions. The above effect was therefore explained as a manifestation of the higher reactivity (by a factor of 100) of ions with track electrons, relatively to H_3O^+ cations.

3. Results and discussion

On the basis of the above experimental data, it was natural to expect that, in EMS experiments, nitrate anions would also exhibit a much higher reactivity with the Auger blob electrons (both hot and quasi-free) than the hydroxonium ions, H_3O^+ , thus strongly inhibiting the reduction of $^{57}\text{Fe}^{3+}$ ions into $^{57}\text{Fe}^{2+}$. However, fitting the data shown in Fig. 1, we have obtained that NO_3^- ions scavenge blob electrons more efficiently than H_3O^+ , ClO_4^- , and HSO_4^- ions, but only by a factor of 3 [8]. This fact strongly contradicts the above mentioned radiation chemical literature data.

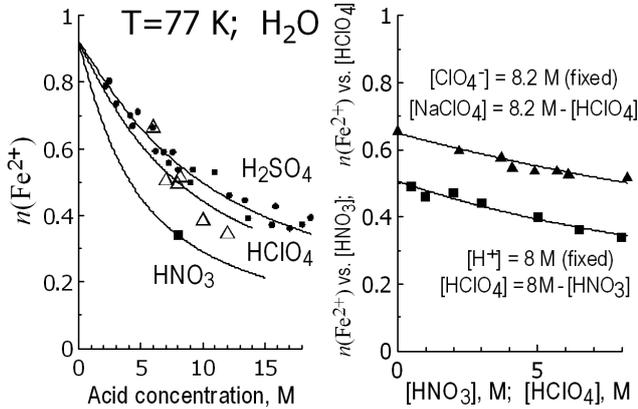


Fig. 1. Dependences of the yields of the Mössbauer ions Fe^{2+} vs. concentration of acids in water (left figure). Right figure — the same dependences, but in solution of salts and acids (▲ — concentration of ClO_4^- ions is fixed; ■ — fixed concentration of H^+ ions). All the measurements were done at 77 K. Solid lines are drawn according to the model developed in [8].

Below we are giving a qualitative explanation to such an unexpectedly small difference in the trapping rates

of quasi-free electrons by NO_3^- and H_3O^+ ions in the Auger blob and discuss other physical issues of the EMS experiment [8]. From the data shown in Fig. 1 one may conclude the following:

1) in the “ideal” case of pure frozen water almost all ($\approx 90\%$) $^{57}\text{Fe}^{3+}$ ions are reduced to the divalent state Fe^{2+} . Unfortunately, this case (pure water) cannot be investigated experimentally, because pure water, when frozen, does not form a homogeneous amorphous ice, but forms a spatially non-homogeneous polycrystalline frozen structure, which is poorly reproducible experimentally;

2) the fraction of reduced iron ions decreases monotonously by adding H_3O^+ , ClO_4^- , HSO_4^- , and NO_3^- . Most probably the dissolved ions weakly capture thermalized quasi-free electrons of the Auger blob (interaction of these ions with “hot” electrons is unlikely). It should be also noted that EMS experiments give an information about intratrack radiolytic processes limited by the half-life of the excited $^{57}\text{Fe}^*$ Mössbauer nucleus ($T_{1/2} = 98$ ns). During this time, most of the track electrons remain not yet localized (their characteristic localization time is > 100 ns);

3) scavenging of secondary track electrons by NO_3^- ions, contrary to the case of liquid water, is rather weak. The nitrate ions react with them only three times more efficiently than H_3O^+ ions. Actually this conclusion does not rely just on the only one experimental point shown in Fig. 1 (left plot) for HNO_3 . There are additional data in the right plot (solutions of HNO_3 and HClO_4 when total concentration of H^+ ions is fixed). So from the statistical viewpoint our conclusion is reliable;

4) as follows from the above mentioned estimation of the radius of the Auger blob (≈ 100 Å) and the number of ion–electron pairs (200–300) therein [2], the concentration c_0 of the secondary quasifree electrons in the blob comes out to be ≈ 0.1 M. If, during the lifetime of the Mössbauer nucleus ($T_{1/2} \approx 10^{-7}$ s), a significant variation of the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ takes place, the reaction rate constant k_{e3} (quasi-free electron capture by Fe^{3+} ion) can be estimated from the relationship $k_{e3}c_0T_{1/2} \approx 1$ (which gives $k_{e3} \approx 10^8$ 1/M/s). Similarly it is possible to estimate the capture rate constants k_{eS} of the quasi-free electrons with the scavengers added into the frozen solution: $k_{eS}c_S T_{1/2} \approx 1$. Since $c_S \approx 10$ M, we obtain $k_{eS} \approx 10^6$ 1/M/s. Therefore, it turns out that the rate constant of the electron capture by Fe^{3+} ion is hundred times greater than the corresponding rate constants for other electron acceptors (a more accurate estimation based on the model [8] leads to a factor of 50). Let us note that, in the case of nitrate ions in liquid water, a similar quantity can be estimated from the relationship $k_{e,\text{NO}_3^-} \approx 1/(c_{37}t_{\text{aq}}) \approx 10^{12}\text{--}10^{13}$ 1/M/s, where $t_{\text{aq}} = 0.3$ ps is the electron hydration time and for nitrate ion $c_{37} = 0.5$ M.

4. Conclusion

In conclusion, three questions have to be answered.

1) What is the reason of such a drastic decrease of the scavenging ability of NO_3^- anions in a frozen matrix in

comparison with the liquid phase? Answer: usually the reaction rate constant (of the electron capture by a scavenger) is large, if (i) the energy of the initial state, $S+e^-$, is close to the energy of the final state S^- (i.e., no energy mismatch) and (ii) the reaction is not accompanied by a considerable structural reorganization of the medium. Seemingly such a situation is realized in the case of pre-solvated electron capture by nitrate ions in liquid water, where this process is rather effective. When the aqueous medium is frozen, the ground state energy of the quasi-free electron V_0 becomes larger by 1 eV as compared to a liquid phase [9] (the same effect occurs not only in water, but in hydrocarbons and alcohols as well). This results in a notable energy mismatch between the energies of the initial and final states, which probably significantly weakens the efficiency of the electron capture by NO_3^- in frozen solutions.

2) Why, for EPR experiments in the same system (nitrate ions in frozen 5 M HClO_4 aqueous solutions) [7], a very large value of the reaction rate constant k_{e,NO_3^-} was obtained? Answer: in EMS experiments one may observe only the initial stage of the intratrack processes, limited by the lifetime of the Mössbauer nucleus ($\leq 10^{-7}$ s for ^{57}Fe). Part of the quasi-free electrons in the Auger blob succeed in recombining with H_3O^+ ions and form an electronically excited state H_3O^* . Other blob electrons are localized in structural traps, which are present in a frozen matrix in a high concentration (≈ 1 M), and then can tunnel to the H_3O^+ ions. This reaction is energetically favorable, but may take much longer time (about an hour). However, this process not always leads to the formation of a hydrogen atom. The matter is that the formation of radiolytic hydrogen is a process of the electron dissociative capture. It means that firstly, the encounter of an electron and H_3O^+ ion produces an electronically excited state H_3O^* , secondly, this state decays into H and H_2O . However, the second step is possible only if the initial H_3O^+ ion disposes of some free volume, sufficient for the H-atom detachment. In a frozen matrix only a small fraction of H_3O^+ ions possesses such a free volume. Therefore, the electron has to migrate (tunnel) from H_3O^+ ion to another, in search of one with the necessary free space. This substantially elongates the kinetics of H-atom formation, so that surrounding NO_3^- ions, although present in a small concentration, have enough time to intercept these electrons (loosely bounded in electronically excited molecules H_3O^*) and thereby suppress the formation of atomic hydrogen. Because the experiment [7] was done with the help of EPR technique, such a long lasting tunneling stage was available for experimental observation [10, 11].

3) Why the k_{e3} comes out approximately 100 times higher than k_{eS} ? Answer: it should be taken into account that around the very swiftly formed chemically

stable $^{57}\text{Fe}^{3+}$ ion, a rather large positive charge ($+ne$) still remains. This charge was originally produced on the primary multicharged $^{57}\text{Fe}^{n+}$ ion (because of emission of the Auger electrons) and then partially transferred to surrounding water molecules forming adjacent H_2O^+ ions. Nevertheless, this large positive charge $+ne$ ($n \approx 5$ in average) strongly attracts secondary quasi-free electrons to the center of the Auger blob, where Fe^{3+} is located (the screening effect). Concentration of the blob electrons on the Fe^{3+} ion increases by a factor of $\sim n^3 \approx 10^2$, which makes all capture rate constants, k_{e3} and k_{eS} , approximately equal.

Finally, we conclude that a likely reason of the discrepancy between radiation chemical data [7] and that obtained by EMS [4, 5, 8] is that the data in [7] correspond to the long-lasting post-radiation (tunneling) processes occurring at much longer times than those in EMS measurements, which are limited to the lifetime of a Mössbauer nucleus and thus describe fast intratrack radiolytic processes.

Acknowledgments

The authors thank Dr. G. Duplâtre for stimulating discussions. This work is supported by the Russian Foundation for Basic Research (grant 11-03-01066).

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