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Radiation-Induced Transformations of 2-Fluoroethanol in Aqueous Solutions

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Abstract—Steady-state radiolysis has been used to study the radiation-induced transformations of 2-fluoroethanol in dilute aqueous solutions as a model system for examining the autoradiolytic dehalogenation of the radiopharmaceutical drug 2-[^{18}F]fluorodeoxyglucose ([^{18}F]FDG). A derivatization—gas chromatography procedure for determining the fluoride anion in the presence of organofluorine compounds has been developed. It has been established that $\cdot$OH and H$\cdot$ induced the dehalogenation of 2-fluoroethanol in aqueous solutions. Unlike bromo- and chlorohydrins, 2-fluoroethanol does not interact with e^-_{aq} according to the dissociative attachment mechanism. It has been shown that O_2 halved the radiation-chemical yield of fluoride due to the oxidation of hydroxyl-containing carbon-centered radicals of 2-fluoroethanol. The constant of unimolecular dehalogenation of the 2-fluoroethanol radical is 3.9×10^6 s^{-1}, as calculated using the method of competing reactions.

Keywords: steady-state radiolysis, dehalogenation, fluoride, 2-fluoroethanol, FDG

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INTRODUCTION

Radiolysis of organofluorine compounds in aqueous solutions still has remained a poorly studied area of high-energy chemistry, although radiation-induced processes involving this group of substances are of great practical importance. Thus, the electron-beam irradiation of polyfluorinated compounds (for example, perfluorooctanoic acid) in solutions and in complex dispersed systems (soil) is considered as an industrial technology for the treatment of these persistent organic pollutants [1]. The radiation-induced transformation of labeled compounds under the influence of their own radiation—autoradiolysis—is a serious problem for the manufacturers of radiopharmaceuticals labeled with the fluorine-18 isotope [2]. In most cases, this process is accompanied by the elimination of the [^{18}F]fluoride anion, which is accumulated in the bone tissue and hence is of high radiobiological hazard.

For 2-[^{18}F]fluoro-2-deoxy-D-glucose ([^{18}F]FDG), which is the most widespread radiopharmaceutical for the diagnosis of cancer, cardiac, and neurological diseases by positron emission tomography (PET) [3], the accumulation of radiolytic fluoride is a key factor limiting the shelf life of the finished dosage form [4]. At high initial volumetric activities of [^{18}F]FDG, which provide the lowest production cost [5], the drug becomes unsuitable for diagnostic use as early as 1 h after synthesis [6].

The studies of autoradiolysis [4, 6–8] and the tests of stabilizers [6, 8] are actively underway in order to improve the quality of the radiopharmaceutical drug and increase its shelf life. However, the identification of nonradioactive products of the decomposition of [^{18}F]FDG and the establishment of the autoradiolysis mechanism of this labeled compound are difficult tasks due to the high radioactivity of commercial radiopharmaceutical batches (to several Sv/h) and nanomolar concentrations of the radioactive substance in solution [9]. To solve the above problems related to studying the autoradiolysis of radiopharmaceuticals, we propose to use steady-state radiolysis of model compounds and a nonradioactive copy of [^{18}F]FDG.

In this work, we will consider the radiation-induced transformations of the simplest fluorohydrin, 2-fluoroethanol, in dilute (10^{-3} mol/L) aqueous solutions.

EXPERIMENTAL

The following commercially available substances were used in this study without preliminary purification: 2,4-dinitrophenylhydrazine (DNPH) of 97% purity, 2-fluoroethanol (95%), trimethylchlorosilane, sodium fluoride (99.9%), aqueous 37% formaldehyde solution, hydrochloric acid, glycolaldehyde (>98%), ammonium formate (>99%), and *tert*-butanol from Sigma-Aldrich; potassium hydroxide and perchloric acid from Aplichem; methanol for HPLC (J.T. Baker); and hexane for chromatography (Kriokhim). High-purity acetaldehyde was obtained by the acid hydrolysis of paraldehyde. The primary distillate was dehydrated with Na_2SO_4 for a day and then repeatedly distilled. The dry acetaldehyde thus obtained was poured into ampoules, sealed, and stored at −20°C for no more than five years. Aqueous solutions of 2-fluoroethanol were prepared by a gravimetric method; they were saturated with gases and sealed in ampoules as described previously [10].

Inorganic fluoride in the presence of organofluorine compounds in aqueous solutions was determined using an adapted chemical derivatization/gas chromatography procedure [11]. To 1 mL of an irradiated aqueous solution of 2-fluoroethanol, which was previously cooled in an ice bath, 2.5 mL of a 1.2 M HCl solution and 20 μL of trimethylchlorosilane were added. The resulting mixture was thoroughly stirred in an ultrasonic bath with ice for 5 min. The resulting fluorotrimethylsilane was extracted with 980 μL of hexane in an ultrasonic bath for 5 min in the cold. A 600-μL portion of the upper organic layer was taken for gas-chromatographic analysis. The resulting solution can be stored for up to a day in a tightly closed vial at +4°C.

Quantitative analysis for fluorotrimethylsilane was performed on a Shimadzu GC-17AAF/APC instrument with an RTX502.2 column. The analysis conditions were the following: initial column temperature, 40°C; isothermal holding for 2 min followed by heating to a temperature of 200°C at a rate of 6°C/min; injector temperature, 220°C; detector temperature, 250°C; carrier gas (nitrogen) velocity, 21 cm/s; and injected sample volume, 1 μL. The concentration was determined by an external standard method. The experimentally determined limit of detection of the fluoride anion in the presence of high concentrations of organofluorine compounds was no lower than 1×10^{-6} mol/L, and the linearity range was 2.5×10^{-6}–2.5×10^{-4} mol/L.

The carbonyl products of 2-fluoroethanol radiolysis were analyzed in the form of adducts with DNPH (hydrazones) on a Shimadzu LCMS-2020 chromatograph with a Shim-pack VP-ODS C18 column 150 mm long and photo diode array (PDA) and mass-spectrometric detectors connected in series. The conditions of the chromatographic analysis were the following: mobile phase, methanol–water in a ratio of 70 : 30 by volume; eluant flow rate, 0.8 mL/min; oven temperature, 35°C; and injected sample volume, 1 μL. Quantitative analysis was performed based on the absorbance of adducts with DNPH at 366 nm using external standards of carbonyl compounds. Hydrazones were identified by mass spectrometry under the following conditions: electrospray ionization (ESI) in the negative ion mode; interface voltage, 1.5 kV; detector voltage, 1.20 kV; heating and desolvation block temperatures, 400 and 250°C, respectively; and atomizer gas flow rate, 1.5 L/min.

To prepare a derivatizing reagent, 0.03 g of DNPH and 6.2 mL of concentrated hydrochloric acid were introduced into a 100-mL volumetric flask, and the contents were brought to the mark with methanol. To obtain the hydrazones of carbonyl compounds, the test samples were mixed with the derivatizing agent in a 1 : 1 volumetric ratio and kept for 15 min before analysis.

The concentration of 2-fluoroethanol in solution was determined by gas chromatography on a Shimadzu GC-17AAF/APC instrument with an RTX-Wax capillary column and a flame-ionization detector; the analysis conditions were similar to those described previously [10]. Hydrogen peroxide was analyzed using a reagent photometric method with $TiOSO_4$ according to Brinkevich et al. [12].

The samples were irradiated on an MRKh-γ-25M unit with a ^{60}Co source at a temperature of 20 ± 5°C. The dose rate was 0.148 ± 0.008 Gy/s according to the results of dosimetry with a Fricke ferrosulfate system. The range of absorbed doses was 0.089–1.066 kGy. The results of at least three independent experiments were used to obtain the radiation-chemical yields. The determination errors of radiation-chemical yields were calculated by the least-squares method with a confidence level of 0.95 using Origin 8.1 Pro software.

RESULTS AND DISCUSSION

Table 1 summarizes the radiation-chemical yields of the radiolysis products of 2-fluoroethanol in aqueous solutions with a concentration of 10^{-3} mol/L obtained in this work. Note that dehalogenation is the main type of radiolytic transformations of the test substance, and the yield of the fluoride anion and, to a lesser extent, the yield of decomposition of the test substance strongly depended on the conditions of irradiation. We detected formaldehyde, acetaldehyde, and glycolaldehyde as minor radiolysis products.

In deaerated aqueous solutions of 2-fluoroethanol, the yield of the fluoride anion is consistent with $G_{\bullet OH}$ and noticeably higher than corresponding values for inorganic phosphate upon the irradiation of 1 mM aqueous solutions of 1-glycerophosphate and glucose 1-phosphate (2.23 ± 0.07 and 2.00 ± 0.07 ion/100 eV, respectively [13]). At the same time, the constants of free-radical dephosphorylation of hydroxyl-containing organic phosphates are considered among the highest for monoradical radiation-induced processes.

Radiolysis of the test substance in a deaerated 0.1 M aqueous solution of *tert*-butanol makes it possible to quantitatively convert •OH radicals into less

Table 1. Yields of the products of radiation-induced transformations of 2-fluoroethanol in aqueous solutions with a concentration of 10^{-3} mol/L

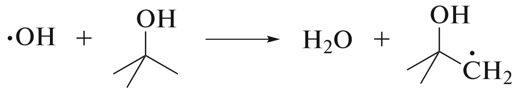
Radiation-chemical yields, molecule/100 eV		Irradiation conditions			
		Ar	t-BuOH + Ar	N_2O	O_2
Decomposition of 2-fluoroethanol		2.58 ± 0.27	1.72 ± 0.71	4.54 ± 0.44	2.13 ± 0.75
Radiolysis products	Fluoride anion	2.79 ± 0.18	0.21 ± 0.03	3.18 ± 0.30	1.43 ± 0.26
	Acetaldehyde	0.14 ± 0.02	0.03 ± 0.01	0.13 ± 0.02	0.02 ± 0.01
	Formaldehyde	0.04 ± 0.01	0.04 ± 0.01	0.14 ± 0.01	0.61 ± 0.06
	Glycolaldehyde	0.05 ± 0.01	0	0.17 ± 0.04	0.30 ± 0.04
	Hydrogen peroxide	0.35 ± 0.07	0	1.00 ± 0.09	2.38 ± 0.12

reactive carbon-centered radicals (I) according to reaction (4). Under these conditions, a more than tenfold decrease in the radiation-chemical yield of fluoride was observed in comparison with that in the system without t-BuOH. This fact is indicative of a low probability of the dissociative attachment of a hydrated electron, which is characteristic of chlorinated, brominated, or iodinated organic compounds, according to reaction (5).

$$H_2O \rightsquigarrow H_2O^{\bullet\oplus} + e^{\ominus}_{aq} \tag{1}$$

$$H_2O^{\bullet\oplus} + H_2O \longrightarrow HO\bullet + H_3O^{\oplus} \tag{2}$$

$$e^{\ominus}_{aq} + H_3O^{\oplus} \longrightarrow H\bullet + H_2O \tag{3}$$



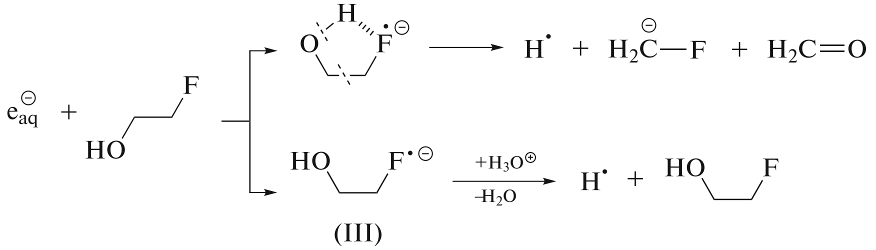
(I)

(4)

$$e^{\ominus}_{aq} + R{-}Hal \longrightarrow \underset{(II)}{R{-}Hal^{\bullet\ominus}} \longrightarrow \underset{Hal\,=\,Cl,\,Br,\,I}{R^{\bullet} + Hal^{\ominus}} \tag{5}$$

Note that the introduction of a scavenger of • OH radicals into the solution led to only a 30% decrease in the radiation-chemical yield of decomposition of 2-fluoroethanol in comparison with that in the deaerated system. Consequently, hydrated electrons, • H, and *tert*-butanol radicals (I) are able to interact with 2-fluoroethanol to result in the consumption of the test compound but mainly without the formation of the fluoride anion.

In a monograph by Dzhagatspanyan and Filippov [14] devoted to the radiation chemistry of organohalogen compounds, it was indicated that organofluorine compounds scavenge solvated electrons and their carbon skeleton can be destroyed as a result of this. We cannot exclude the occurrence of such a process (for example, reaction (6)) because the introduction of *tert*-butanol into the system did not change the radiation-chemical yield of formaldehyde, as compared to that in deaerated solutions. However, taking into account the value of $G(CH_2O)$, the neutralization of radical anion (III) with H_3O^+ by reaction (7) is much more probable.



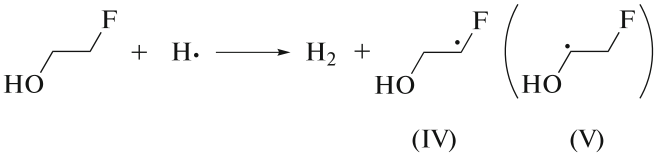
(III)

(6)

(7)

The •H species formed in the course of reaction (7) can interact with 2-fluoroethanol to predominantly form α-fluoromethyl radicals (IV) and, to a lesser extent, α-hydroxymethyl radicals (V) according to reaction (8). A similar reaction with the participation of *tert*-butanol radicals (I) also cannot be ruled out.

Because no glycolaldehyde is formed in the presence of *tert*-butanol, we can state that α-fluoromethyl radicals (IV) do not undergo hydrolysis under these experimental conditions. This is due to a low rate of hydrolysis of α-fluoromethyl radicals (IV) and the reducing properties of intermediates dominating in the system (e^-_{aq}, •H, and radicals (V)). In our opinion, fluoride anions are formed with a low yield in the radiolysis of 2-fluoroethanol in the presence of a scavenger of •OH radicals only as a result of free-radical fragmentation of radicals (V) according to reaction (9). Previously, it was shown that similar reactions lead to the radiation-induced dehalogenation of various bromo- and chlorohydrins in aqueous solutions [15].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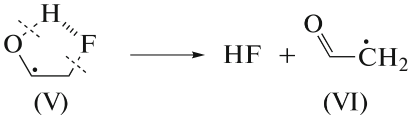

(9)

The subsequent reduction of radicals (VI) leads to the formation of acetaldehyde, which was detected as a final molecular product of the radiolysis of 2-fluoroethanol in all the systems studied in this work.

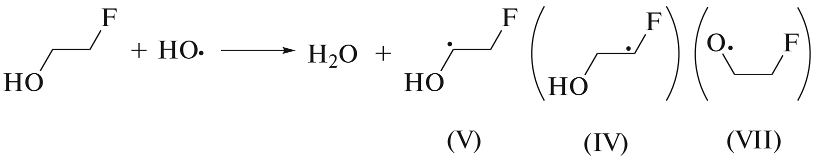
In conclusion of a consideration of the system, note that the relatively low radiation-chemical yields of the fluoride anion in the radiolysis of 2-fluoroethanol in the presence of *tert*-butanol are also related to the ability of this scavenger to interact with •H in a reaction similar to (4), as a result of which the probability of reaction (8) with the formation of radicals (V) decreases.

The saturation of aqueous solutions with nitrous oxide led to a doubling of the yield of •OH upon radiolysis and the removal of hydrated electrons from the system due to reaction (10). However, the data given in Table 1 indicate that with an almost twofold increase in the radiation-chemical yield of decomposition of 2-fluoroethanol in the presence of N_2O in comparison with that in the deaerated system, only a 15% increase in the radiation-chemical yield of inorganic fluoride was observed.

This experimentally detected fact can be associated with the following circumstances: First, the dehalogenation of 2-fluoroethanol in a solution saturated with argon was caused, in particular, by interaction with the hydrated electron due to the above sequence of reactions (7)–(9). Therefore, the removal of e^-_{aq} from the system leads to the exclusion of one of the pathways for the formation of the fluoride anion. Second, due to a low concentration of 2-fluoroethanol, a portion of •OH in the solution volume was consumed in biradical rather than radical–molecule reactions with the test substance, as evidenced by $G(H_2O_2) > G_{H_2O_2}$ (Table 1).

The interaction of 2-fluoroethanol with •OH, in addition to carbon-centered radicals (IV) and (V), also leads to the formation of oxygen-centered radical (VII). The latter undergoes β-fragmentation via reaction (12) with carbon–carbon bond rupture, which manifested itself in an increase in the radiation-chemical yield of formaldehyde, as compared with that in the argon-saturated solution.

$$e_{aq}^{\ominus} + N_2O + H_2O \longrightarrow {\cdot}OH + N_2 + HO^{\ominus} \qquad (10)$$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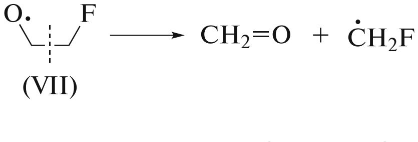
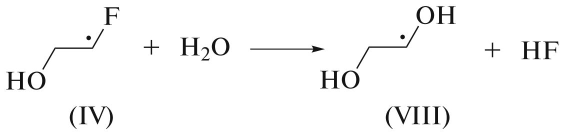
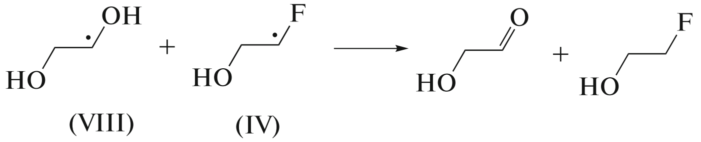

(12)

The main sources of inorganic fluoride on the radiolysis of 2-fluoroethanol in a solution saturated with N_2O are α-hydroxyl-containing carbon-centered radicals (V) capable of eliminating hydrogen fluoride by reaction (9).

It is likely that glycolaldehyde is mainly formed under these conditions due to the hydrolysis of α-fluoromethyl-type radical (IV) according to reaction (13). Ethylene glycol radical (VIII) formed in reaction (13) can be oxidized to glycolaldehyde in disproportionation reactions with carbon-centered radicals present in the system, for example, by reaction (14).

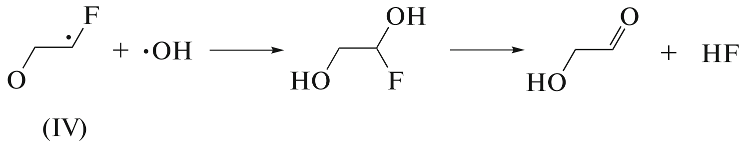


(13)



(14)

Due to a low concentration of 2-fluoroethanol in solution, the possibility of the formation of glycolaldehyde cannot be completely ruled out as a result of the combination of • OH with α-fluoromethyl-type radicals (IV) and acetaldehyde radicals (VI) in accordance with the following reactions:



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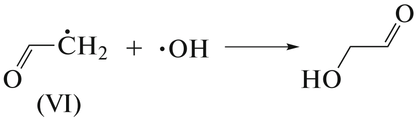


(16)

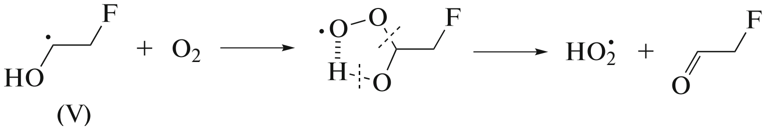
In oxygen-saturated aqueous solutions of 2-fluoroethanol, hydrated electrons and hydrogen atoms interact with O_2 according to reactions (17) and (18), as a result of which these radical products of water radiolysis are quantitatively converted into $O_2^{\bullet-}$ at pH ~ 7.

$$e_{aq}^{\ominus} + O_2 \longrightarrow O_2^{\bullet\ominus} \tag{17}$$

$$H^{\bullet} + O_2 \longrightarrow HO_2^{\bullet} \tag{18}$$

$$HO_2^{\bullet} + H_2O \rightleftarrows O_2^{\bullet\ominus} + H_3O^{\oplus} \quad pKa = 4.8 \tag{19}$$

Therefore, the radiation-induced transformations of 2-fluoroethanol in oxygen-saturated aqueous solutions are due to the interaction of this fluorohydrin with • OH and $O_2^{\bullet-}$ radicals, which exhibit oxidizing properties. The twofold decrease in the radiation-chemical yield of inorganic fluoride observed under these conditions in comparison with that in the solution saturated with argon can be partly due to the removal of • H from the system and, as a consequence, the impossibility of reaction (8). However, only a slight decrease in the radiation-chemical yield of decomposition of 2-fluoroethanol and a several-fold decrease in the yield of acetaldehyde indicate that the dehalogenation of the test substance can be inhibited because of the oxidation of α-hydroxyl-containing carbon-centered radicals (V) by oxygen according to the following reaction:

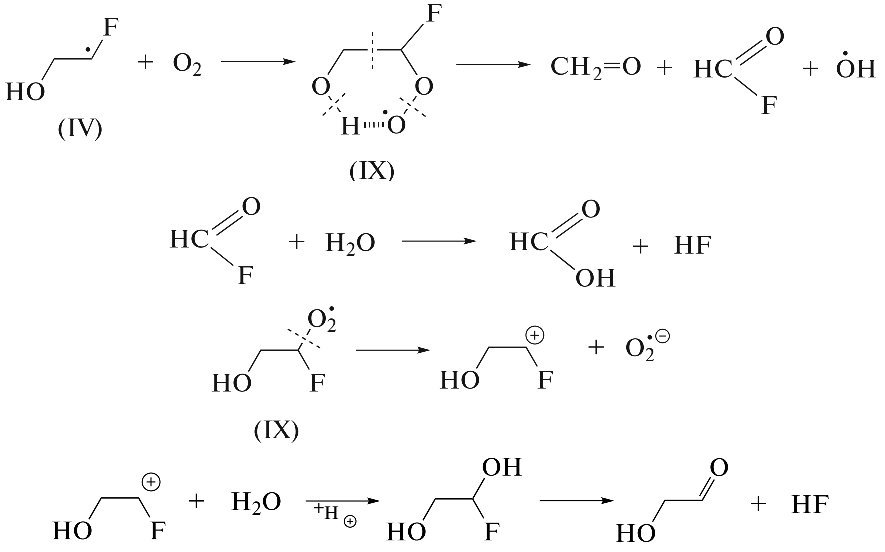


(20)

A process similar to reaction (20) on the storage of the radiopharmaceutical drug 2-[^{18}F]fluorodeoxyglucose may be responsible for the inhibition of its autoradiolytic decomposition in the presence of oxygen, which was observed by Brinkevich and Tugai [7].

Unfortunately, we were unable to identify 2-fluoroacetaldehyde as a radiolysis product of 2-fluoroethanol; this can be due to both the limitations of the analytical procedure and the high reactivity of this halogen-containing aldehyde under radiolysis conditions.

An increase in the radiation-chemical yields of formaldehyde and glycolaldehyde in the radiolysis of oxygen-saturated solutions of 2-fluoroethanol is due to the interaction of α-fluoromethyl-type radicals (IV) with oxygen. A reaction similar to (21) was previously observed in the case of irradiation of α-diols in aqueous solutions saturated with oxygen [15]. The elimination of $O_2^{\bullet -}$ by peroxyl radicals was found previously in the radiolysis of disaccharides in the presence of oxygen [16].



(21)

(22)

(23)

(24)

Despite the formation of additional amounts of inorganic fluoride in reactions (22) and (24), its radiation-chemical yield in oxygenated solutions of 2-fluoroethanol was lower than that in deaerated solutions by a factor of approximately 2. This fact indicates a high efficiency of oxygen inhibition of the free-radical dehalogenation of 2-fluoroethanol (reaction (9)) due to the oxidation of its α-hydroxyl-containing carbon-centered radicals (V) according to reaction (20).

The radiation-chemical yields of the fluoride anion obtained in this work upon the radiolysis of the test substance under various conditions allowed us to estimate the rate constant of the monoradical dehalogenation (reaction (9)) of 2-fluoroethanol. If we assume that inorganic fluoride is formed only from α-hydroxyl-containing carbon-centered radicals (V), the elimination of the fluoride anion inhibited by 50% in the presence of oxygen indicates the equality of the reaction rates of the oxidation of radical (V) with oxygen according to reaction (20) and the monoradical dehalogenation of this radical by reaction (9):

$$k2 \times [R\bullet] \times [O_2] = k1 \times [R\bullet]. \qquad (25)$$

Then, taking into account the concentration of oxygen in solution (1.22 × 10^{-3} mol/L) [17] and a rate constant of 3.2 × 10^9 L mol^{-1} s^{-1} for the addition of oxygen to radical (V) (a constant of the interaction of O_2 with ethylene glycol radical (VIII) reported by Adams and Willson [18] was taken), we obtain the rate constant of monoradical dehalogenation of 2-fluoroethanol

$$k1 = k2 \times [O_2] = 3.904 \times 10^6 \text{ s}^{-1}. \qquad (26)$$

This value is more than four orders of magnitude higher than the rate constant of dehydration of ethylene glycol radicals (VIII) and approximately equal to the rate constant of dephosphorylation of a lysophosphocholine radical (3.5 × 10^6 s^{-1} [19]).

CONCLUSIONS

The mechanism and final molecular products of the radiation-induced transformations of 2-fluoroethanol in dilute aqueous solutions as a model of autoradiolytic dehalogenation of the radiopharmaceutical drug 2-[^{18}F]fluorodeoxyglucose were studied using steady-state radiolysis. A derivatization–gas chromatography procedure for the determination of the fluoride anion in the presence of organofluorine compounds was developed. It was found that the dehalogenation of 2-fluoroethanol in aqueous solutions is due to its interactions with OH • and H •. In this case, the addition of e^-_{aq} does not lead to the elimination of fluoride, which distinguishes the radiation chemistry of 2-fluoroethanol from that of hydroxyl-containing organochlorine and organobromine compounds. It was shown that the main mechanism of the radiation-induced dehalogenation of 2-fluoroethanol in aqueous solutions is the free-radical fragmentation of its hydroxyl-containing carbon-centered radical accompanied by the breaking of two σ bonds in the β-position to the radical center. Oxygen decreases the radiation-chemical yield of inorganic fluoride by a factor of about 2 due to the oxidation of the hydroxyl-containing carbon-centered radical of 2-fluoroethanol. The calculated reaction rate constant of the monoradical dehalogenation of 2-fluoroethanol is $3.9 \times 10^6\ s^{-1}$.

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