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Bis(octafluoropentoxy)methane: aspects of radiolysis at high absorbed doses

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Liquid products such as light alcohols, ethers, hydrocarbons, HF and high-molecular-weight compounds, as well as gases, were detected in the radiolysis of bis(octafluoropentoxy)methane.

Fluorohydrocarbons are of interest as diluents for radiochemical processing due to their chemical stability, flame resistance, low viscosity and small toxicity.[1–3] For example, heavy fluorinated diluents are promising for the replacement of perchlorobutadiene, which is widely used in radiochemistry.[3] Thus, the fluorinated organic compounds should have high radiation-chemical stability to be appropriate for radiochemistry.

We studied the radiolysis of bis(2,2,3,3,4,4,5,5-octafluoropentoxy)methane $CH_2[OCH_2(CF_2)_3CF_2H]_2$ (Formal-2).[†] This compound contains a high electronic fraction of fluorine (61.5%) and belongs to the class of acetals (geminal diethers). Acetals can be produced by the interaction of aldehydes with alcohols in the presence of acids.[4] Acetals are more resistant to the action of alkalis and oxidizers than free aldehydes. Compounds containing an aldehyde group are often converted into acetals to protect this group during synthetic operations.[4,5] Alternatively, the formation of acetals in the presence of water and acid is reversible: an aldehyde and an alcohol are formed again in acetal hydrolysis. Hydrolysis does not occur under alkaline conditions. Radiolysis of gaseous fluorohydrocarbons is discussed in the literature.[6–9] However, the resistance of acetals to irradiation was practically not studied.

Deaerated samples of Formal-2 were investigated. A sample had a specific gravity of 1.55 g cm^{-3} and contained ≥ 99.6 wt% Formal-2. Initial Formal-2 has a low index of refraction (n_D^{20} 1.3258). The dependence of n_D^{20} on absorbed dose D was linear; $n_D^{20} = 1.3258 + 6.9\times10^{-6}D$ (curve *1* in Figure 1). Such an effect can be observed when the fraction of F atoms in the liquid is being decreased as in the case of fluoroalkyl fragments elimination and their further transformations into volatile compounds.

The above increase in refraction index is in a good agreement with gaseous radiolytic product formation (Figure 2, curve *4*). The gassing being rather plentiful is observed even after termination of irradiation. The main light products of radiolysis are fluoroalkenes and fluoroalkanes C_1–C_3. Such gases as C_3HF_5, C_2F_4 and C_2HF_3 prevail among alkenes. These products are formed as a result of C–C bond cleavage in fluoropentyl groups of Formal-2. The partial or complete replacement of H atoms by F in alkanes and alkenes C_1–C_5 is known[1,2] to increase their volatility. Thus, any fluorohydrocarbon received by radiolytic cleavage of C–C bond in Formal-2 is gaseous. The fluorinated ethers (mainly, methyl ethyl and methyl propyl ethers) and the fluorinated methanol CH_2FOH are also detected among volatile products. Thus, there are a lot of light radiolytic products containing fluorine. Their volatilization results in decrease of F atoms abundance in irradiated liquid.

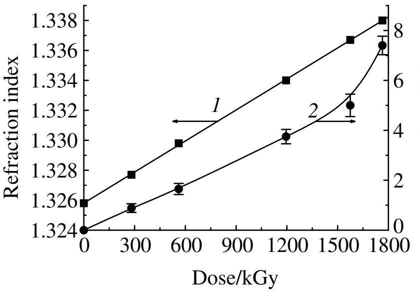

Figure 1 Influence of absorbed dose on (*1*) refraction index of liquid phase and (*2*) acidity in aqueous extract.

Irradiated samples contain 20 liquid radiolytic products with molecular weights less than that of Formal-2 ($M < 476$). The main product is octafluoroamyl alcohol ($C_5H_3F_8OH$, $M = 232$): its fraction exceeds half of the total mass of liquid radiolytic products in all range of absorbed doses (Figure 2, curves *2*, *3*). The observed initial yield of $C_5H_3F_8OH$ formation is 0.29±0.02 μmol J^{-1}. Light products ($M < 232$) are presented by ethers, mostly dissolved volatile ethers; some of them were observed among gaseous radiolytic products. Components with $232 < M < 476$ are the products of fluorohydrocarbon C_1–C_4 fragment elimination from

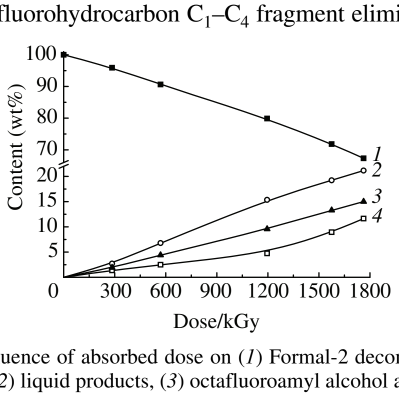

Figure 2 Influence of absorbed dose on (*1*) Formal-2 decomposition and formation of (*2*) liquid products, (*3*) octafluoroamyl alcohol and (*4*) gas.

[†] Formal-2 was kindly given by V. A. Babain from V. G. Khlopin Radium Institute, St. Petersburg.

The radiation source was a U-003 linear accelerator (energy, 8 MeV; pulse duration, 6 μs; pulse repetition frequency, 300 Hz; average beam current, 800 μA). The average dose rate was 1.1 kGy s^{-1}. Poly(methyl methacrylate) DRD 0.4/4 dosimeter was used. The intermittent mode of irradiation was applied to avoid an excessive radiation heating of a sample. The absorbed dose at each stage of irradiation was 9.5 kGy. The radiolytic products were analyzed with a Q-Mass Perkin-Elmer AutoSystem XL gas chromatograph–mass spectrometer (carrier gas, helium; a 60 m glass capillary column 0.25 μm in inner diameter). Refraction indexes were measured by an IRF-454 BM refractometer at 20 °C. An I-500 ion meter was used to define acidity.

Formal-2. The yield of such liquid products does not exceed 0.04 μmol J^{-1}.

Formal-2 radiolysis results in the accumulation of high-molecular-weight compounds. The irradiated samples become turbid and their viscosity increases. Their outlet velocity from a microcapillary decreases while the absorbed dose increases (Figure 3). At 1.76 MGy the liquid becomes approximately six times more viscous than Formal-2. The dose dependence of the accumulation of high-molecular-weight compounds is non-linear. Unirradiated Formal-2 is a water-insoluble compound: prompt phase separation is observed in mixtures of water with Formal-2. In turn, shaking of irradiated Formal-2 with water produces a gelatinous mass; in this case, unmixing is retarded considerably. Apparently, the formation of high-molecular-weight compounds is caused by both condensation involving unsaturated products and macroradicals recombination.

Formal-2 radiolysis results in HF formation. Acid concentration at a dose of 1.76 MGy is almost 1 mol dm^{-3}. Hydrofluoric acid can attack olefinic bonds[1–3] and the observed yield of unsaturated compounds is reduced.

Partial HF redistribution into aqueous phase is observed at shaking water with irradiated Formal-2. Figure 1 (curve *2*) indicates that the aqueous phase is acidified.

HF accumulation has a negative influence on the Formal-2 stability because of acetal decay *via* acid catalysis:[4,5]

$$\mathrm{ROCH_2OR} \xrightleftharpoons{\mathrm{H^+}} \mathrm{ROH + ROCH_2^+} \xrightleftharpoons{\mathrm{H^+,\,H_2O}} \mathrm{2ROH + CH_2O} \quad (1)$$

Fluorohydrocarbons, as well as other organic halides, are effective electron scavengers.[6,7] Dissociative capture of a secondary electron by Formal-2 leads to F^- ion abstraction:

$$\mathrm{C_{11}F_{16}H_8O_2 + e^- \longrightarrow C_{11}F_{16}H_8O_2^{\overline{\bullet}} \longrightarrow {\cdot}C_{11}F_{15}H_8O_2 + F^-} \quad (2)$$

F^- ions can be transformed into HF or ·F atoms by the subsequent geminate neutralization. Completely fluorinated Formal-2 seems to be more stable under irradiation because ·F atoms do not abstract fluorine to form F_2 (which has a low bond dissociation energy)[7] but abstract hydrogen to form HF (which has a high bond energy). Molecular fluorine formed by combination of ·F atoms is readily attacked by free radicals (·R):

$$\mathrm{F_2 + {\cdot}R \longrightarrow {\cdot}F + RF} \quad (3)$$

It is known that acyclic ethers are not radiation resistant.[6,7] For example, the yield of ethoxyethane decomposition is 1.13 mol J^{-1}.[7] The destruction of C–O bonds is observed in the mass spectra of ethers.[11] Alkoxy or alkyl radical elimination is of major importance in mass spectra of acetals. Originally formed oxygen-containing fragments can decay further like in the case of aliphatic ethers *via* hydrogen rearrangement and olefine elimination.[10]

Prevailing octafluoroamyl alcohol formation suggests dissociative ionisation with elimination of an alkoxy radical to be the main primary process of Formal-2 radiolysis:

$$\mathrm{H_3F_8C_5{-}O{-}CH_2{-}O{-}C_5F_8H_3 \rightarrow [H_3F_8C_5{-}O{-}CH_2]^+ + {\cdot}OC_5F_8H_3 + e^-} \quad (4)$$

The $\cdot OC_5F_8H_3$ radical abstracts an H atom from a next molecule and transforms into octafluoroamyl alcohol. The cation $[H_3F_8C_5–O–CH_2]^+$ is unstable: the chromatogram of irradiated Formal-2 does not contain peaks due to the product of nondissociative neutralisation of this ion.

According to reaction (2), the F^- ion can participate in cation and cation-radicals geminate neutralisation. Thus, the reaction of ion neutralisation can proceed more slowly than electron-cation pair recombination.[6,7] The reactions of primary cations with solvent, as well as reactions of their rearrangement or fragmentation, can come to the end before geminate neutralisation. In particular, a significant role of fragmentation reactions follows from the high total yield (≈0.4 μmol J^{-1}) of gaseous products of C–C bond cleavage. Most likely, $[H_3F_8C_5–O–CH_2]^+$ cation formed in primary ionization (4) decomposes eliminating fluoroethylene or fluoropropene. If the fluorinated alkenes were formed mainly by excited Formal-2 molecules decay the liquid products with $232 < M < 476$ should be accumulated. But the yield of such liquid compounds is not significant. On the contrary, appreciable accumulation of light oxygen-containing compounds with the reduced length of the fluorohydrocarbon chain is observed.

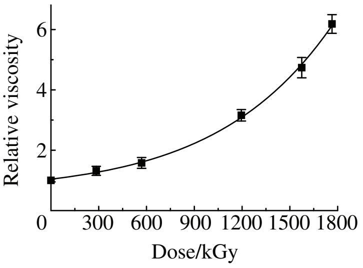

Figure 3 Dependence of relative viscosity on absorbed dose.

In nonfluorinated hydrocarbons a cleavage of C–H bond is also significant. Usually, in nonbranched acyclic hydrocarbons, it occurs more often than C–C bond cleavage.[6,7] Due to exclusively strong C–F bond[1,7] the relative probability of C–C and C–O bond cleavages is increased in fluorochemicals.

As it follows from Figure 2, both Formal-2 decomposition yield *G*(-formal) and main products formation yields increase with absorbed dose. At 0.28–1.76 MGy, *G*(-formal) increases from 0.30 to 0.52 μmol J^{-1} whereas the observed yield of octafluoroamyl alcohol accumulation changes from 0.29 to 0.42 μmol J^{-1}. This effect can be caused by the secondary reactions of radiolytic products. For example, in process of HF accumulation, the role of reaction (1) catalyzed by acid is increased. One of the products of Formal-2 acid-stimulated decomposition is formaldehyde. Probably, fluoromethyl alcohol CH_2FOH is formed from formaldehyde by reactions involving ·F or HF.

Thus, Formal-2 radiolysis leads mainly to cleavage of C–O and C–C bonds. Light alcohols, ethers and hydrocarbons are formed. An important feature of Formal-2 radiolysis is the effective formation of a gas and HF. Formal-2 seems to be unsuitable for high energy processing.

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