

Radiation-chemical effects in the near-field of a final disposal site: role of bromine on the radiolytic processes in NaCl-solutions

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Summary. The oxidation of Br⁻ by Cl₂⁻ is investigated by gamma pulse radiolysis in aqueous solutions of NaCl and NaBr. Depending on the ratio of the concentration of Br⁻ to Cl⁻, the main product being observed is either Cl₂⁻, ClBr⁻ or Br₂⁻. The mixed radical anion ClBr⁻ exhibits a broad absorption band at 350 nm with $\epsilon_{350} = 9300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The rate constants of the equilibrium $\text{Cl}_2^- + \text{Br}^- \rightleftharpoons \text{ClBr}^- + \text{Cl}^-$ are determined to be $k_f = 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_b = 1.1 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The formation of the Cl₃⁻ ($\lambda_{\text{max}} = 220 \text{ nm}$), Cl₂Br⁻ ($\lambda_{\text{max}} = 230 \text{ nm}$) and ClBr₂⁻ ($\lambda_{\text{max}} = 245 \text{ nm}$) ions in the radiation-chemical oxidation of Cl⁻ and Br⁻ ions in an aqueous solution was observed by pulse radiolysis, and its mechanisms of appearance and the equilibrium constants were determined.

Introduction

If brines get access to high level waste forms in a final disposal site in rock salt the radiation will induce the formation of radiolytic products in the solution. Such radiolytic compounds will influence the mobility of radionuclides *via* redox and complex formation reactions and the variation of the pH [1,2]. Radiation effects in chloride brines are therefore of fundamental importance for the safety of a final disposal. The radiolysis of highly concentrated chloride solutions (NaCl, MgCl₂ and LiCl) was previously investigated [3–8]. Using pulse radiolysis it was found that the Cl₂⁻ radical anions are formed in acidic solutions as a consequence of the following reversible reactions:



In neutral or slightly alkaline solutions radical anions Cl₂⁻ were observed only in concentrated solutions (> 0.1 M Cl⁻) where they are formed in acidic spurs and/or as a result of direct action of irradiation on Cl⁻ ions. The

yield of different radiolytic products formed by γ -radiolysis from NaCl brines at ambient temperature and dose rates between 0.1 and 1 kGy/h were determined [9,10]. At a chloride concentration of 6 M NaCl both H₂, O₂ and ClO₃⁻ were formed proportionally to the dose and independently from the dose rate with radiation-chemical yields of 0.6, 0.16 and 0.074 molecules per 100 eV, respectively, *i.e.*: an extended kinetic model for the chloride system which include the formation of chlorate [11] was used to simulate the experimental results [10]. According to this model the chlorate appears as a consequence of the chemical and radiation-chemical redox reactions of hypochlorite. This compound is formed *via* the following reactions:



These reactions show that the action of ionizing radiation on aqueous solutions of chlorides induces consecutive oxidation steps resulting finally in stable compounds. The first, radical step, affords Cl₂⁻. Recombination of these species gives chlorine molecules Cl₂, which exist in equilibrium with the trichloride ions Cl₃⁻. At the second, molecular step, the Cl₂ molecules are hydrolyzed yielding hypochlorous acid, HClO. Then hypochlorous acid and its salts are unstable and undergo further transformations giving rise to chlorites and eventually chlorates. Simultaneously, gaseous hydrogen and oxygen are formed due to water radiolysis.

Natural brines contain many other compounds, first of all bromides. These compounds are expected to influence substantially the reaction scheme and speciation following the initial radiation-induced chemical oxidation of the Cl⁻ ions.

To clarify the situation we have performed pulse radiolysis experiments with highly concentrated chloride solutions containing Br⁻ ions as additives. It was found that bromides have a dramatical effect on the radiolytic oxidation of chlorides in aqueous solution and on the nature of products formed.

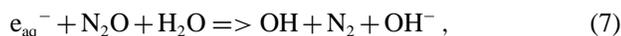
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Experimental

The pulse radiolysis apparatus [12] and the computer programs [13] of the 3.8 MeV van de Graaff accelerator facility ELBENA at the Hahn-Meitner-Institut have been previously described. The duration of the electron pulses ranged from 3 to 20 ns [14]. The optical signals were derived from the average of 10 individual experiments. The absorbed dose per pulse was calibrated by using $\varepsilon = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the e_{aq}^- absorption at 700 nm [15]. The yield of electrons in water at pH = 7 was taken to be 2.6 species per 100 eV of absorbed energy ($0.269 \mu\text{mol J}^{-1}$) [16]. Sodium chloride and bromide (Merck, suprapur) were used after additional recrystallization. Solutions were prepared using triply distilled water and were saturated with N_2O .

Results and discussion

Weakly acidic ($5 \times 10^{-4} \text{ M HCl}$) aqueous solutions of NaCl containing NaBr were studied. By blowing the solution with N_2O , the hydrated electrons e_{aq}^- , formed in the primary processes along with OH, are converted into hydroxyl radicals by the reaction



($[\text{N}_2\text{O}] = 2.6 \times 10^{-2} \text{ M}$ and $k_7 = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [16]. Thus, due to the presence of N_2O , the exposure of water to ionizing radiation results in the predominant generation of OH radicals. The H^+ ions catalyze the oxidation of Cl^- ions by OH radicals in aqueous solutions [4]. The experimental conditions chosen enabled us to exclude further reactions involving e_{aq}^- from considerations and, hence, they markedly facilitate the study of the mechanism of the radiation-induced oxidation of halogens by OH radicals in aqueous solutions.

The formation of radical anions Cl_2^- , ClBr^- and Br_2^-

Fig. 1 a shows the optical absorption spectra of 1 M solutions of NaCl (pH = 3.3) saturated with N_2O and containing $3.2 \times 10^{-4} \text{ M}$ of NaBr after exposure to a 5-ns pulse of accelerated electrons. The high concentration of Cl^- ions ensures that the OH radicals resulting from water radiolysis are captured almost completely by Cl^- rather than by Br^- ions. After the pulse, the typical absorption spectrum of the Cl_2^- with a maximum at 340 nm ($\varepsilon = 8.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) [4] is observed. It can be seen from Fig. 1 a that the optical absorption at shorter wavelengths decreases with time after the pulse, whereas the absorption at longer wavelengths increases. As a consequence, the optical absorption band shifts to longer wavelengths (to approximately $350 \pm 3 \text{ nm}$) and becomes somewhat more intensive (Fig. 1 a). These facts can be reasonably attributed to the reaction of Cl_2^- with Br^- ions. This reaction is fairly fast and in the presence of $3.2 \times 10^{-4} \text{ M}$ NaBr it is virtually completed about 2 μs after the pulse. At longer times, the optical absorption shown in Fig. 1 a decays without noticeable change in the shape of the band. The decay kinetic is described by a second-order rate law. As the concentration of Br^- ions increases

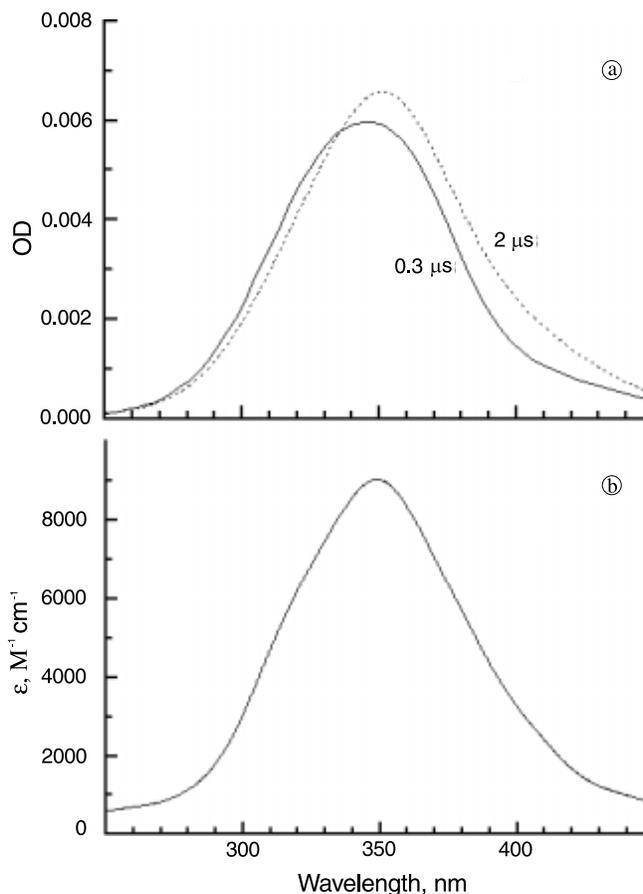


Fig. 1. (a) Absorption spectrum of a 1 M NaCl solution at pH = 3.3, containing $3.2 \times 10^{-4} \text{ M}$ NaBr and saturated by N_2O at different times after the pulse. Pulse duration 5 ns; absorbed dose $8.3 \times 10^{15} \text{ eV/ml}$. (b) Absorption spectrum of ClBr^- .

the new absorption band appears having a maximum at 360 nm and corresponding to the Br_2^- radical anion ($\varepsilon = 9.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) [17]. The whole set of experimental data however indicates that, apart from the Br_2^- , the reaction of Cl_2^- with Br^- gives rise to one more specie whose optical characteristic in the UV region is close to that of Cl_2^- and Br_2^- .

We assume that the species arising in the reaction of Cl_2^- with Br^- apart from Br_2^- is the mixed radical anion ClBr^- . Species of this type, namely ClSCN^- and BrSCN^- radical anions, have been found previously by pulse radiolysis in the oxidation of chloride [18] and bromide [19] ions, respectively, in the presence of small amounts of SCN^- ions. Apparently, the ClBr^- arises and exists in equilibrium with Cl_2^- and Br_2^- via the following reactions:



To describe the oxidation of Br^- ions with Cl_2^- in the solutions studied, a computer simulation of the processes was performed [20]. As a result of the simulation the rate constants of forward ($k_{8f} = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{9f} = 8.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and of the back ($k_{8b} = 1.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$; $k_{9b} = 4.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) reaction were determined. The equilibrium constants of $K_8 = k_{8f}/k_{8b}$ and $K_9 = k_{9f}/k_{9b}$ are equal to 3.6×10^7 and 1.9×10^3 , respectively. From the K_8

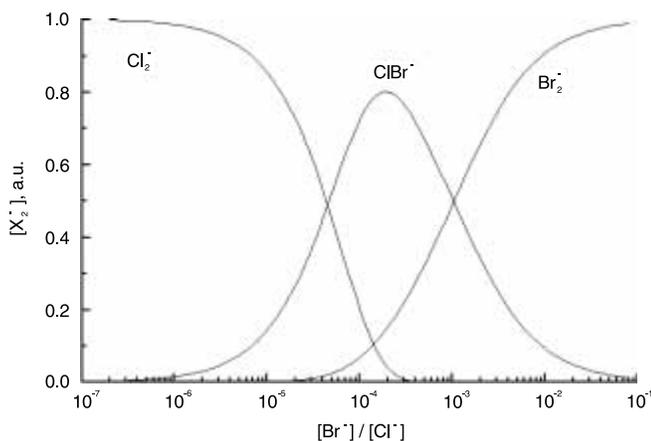


Fig. 2. Calculated dependence of relative concentrations of radical anions on the ratio $[\text{Br}^-]/[\text{Cl}^-]$ at $[\text{Cl}^-] = 1 \text{ M}$.

value, $E^0(\text{ClBr}^-/\text{Cl}^-, \text{Br}^-) = 1.85 \text{ V}$ is obtained, which lies between the redox potentials of Br_2^- (1.66 V) and Cl_2^- (2.30 V) [20].

Fig. 1 b shows the spectrum of ClBr^- . It has a broad absorption band with a maximum at $350 \pm 3 \text{ nm}$; ϵ at this wavelength is $9300 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$. Fig. 2 shows as a result of our calculation the ratio of the equilibrium concentrations of Cl_2^- , ClBr^- , and Br_2^- in the absence of their decay as a function of the Br^-/Cl^- concentration ratio. In concentrated solutions of chlorides, Cl_2^- ions formed are rapidly converted into the bromine-containing species ClBr^- and Br_2^- . Indeed, even in the presence of 10^{-4} M of Br^- ions in a 1 M solution of NaCl, the ClBr^- radical anion predominates. With an increase in the bromide concentration, the proportion of Br_2^- increases. Thus, even at the radical step of radiolysis of concentrated chloride solutions, the presence of bromides affects dramatically the pathway of the chemical processes, which actually result in the oxidation of Br^- ions to give bromine-containing radical anions, ClBr^- and Br_2^- .

The Cl_2^- , ClBr^- and Br_2^- species disappear in a second-order reactions, their half-life ($\tau_{1/2}$) decreases proportionally to the dose of a pulse. This is due to disproportionation reactions similar to reaction (4); eventually halogen molecules which exist in equilibrium with trihalide ions are formed *via* reactions according to Eq. (5).

The disappearance of Cl_2^- and the formation of Cl_3^-

It was found that the decay of Cl_2^- in a 1 M solution of NaCl gives rise to a low-intensity absorption with a maximum at about 220 nm. The signal intensity increases with an increase in the salt concentration in the solution. This optical absorption is observed rather clearly for a 5 M solution of NaCl as illustrated by Fig. 3a. The absorption band with a maximum at 220 nm belongs to the trichloride ion Cl_3^- . Its absorption spectrum as well as that of molecular chlorine in neutral and acidic aqueous solution has already been published [21]. According to this study, the spectrum of Cl_3^- is a broad optical band with a maximum at about 220 nm and $\epsilon = 1.04 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The ϵ value for Cl_2 at 330 nm is smaller than $70 \text{ M}^{-1} \text{ cm}^{-1}$. The related equilibrium constant K_5 amounts to $0.18 \pm 0.02 \text{ M}^{-1}$. In other words, the equilib-

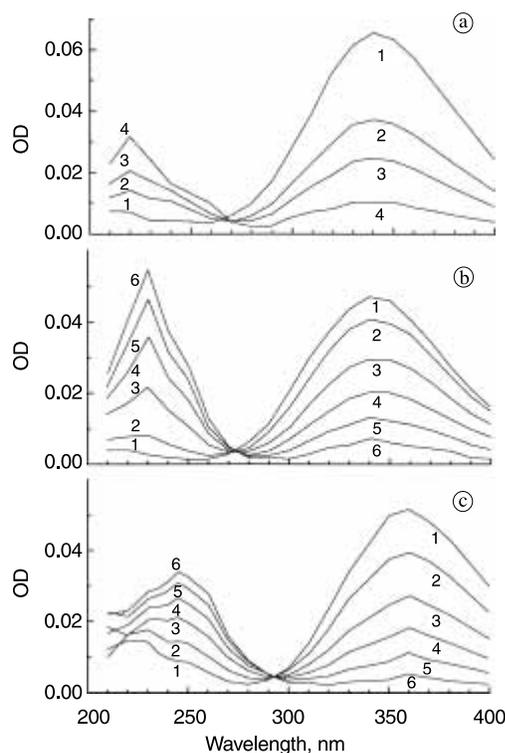


Fig. 3. (a) Absorption spectra of a 5 M NaCl solution at $\text{pH} = 3.3$ saturated by N_2O at different times after the pulse: 1–1 μs , 2–35 μs , 3–80 μs and 4–250 μs . Pulse duration 20 ns; absorbed dose $7.4 \times 10^{16} \text{ eV/ml}$. (b) Absorption spectra of a 1 M NaCl solution at $\text{pH} = 3.3$, containing $1 \times 10^{-3} \text{ M}$ NaBr and saturated by N_2O at different times after the pulse: 1–1 μs , 2–8 μs , 3–24 μs , 4–50 μs , 5–100 μs and 6–250 μs . Pulse duration 20 ns; absorbed dose $5.9 \times 10^{16} \text{ eV/ml}$. (c) Absorption spectra of a 1 M NaCl solution at $\text{pH} = 3.3$, containing $1 \times 10^{-2} \text{ M}$ NaBr and saturated by N_2O at different times after the pulse: 1–1 μs , 2–8 μs , 3–24 μs , 4–50 μs , 5–100 μs and 6–250 μs . Pulse duration 20 ns; absorbed dose $5.8 \times 10^{16} \text{ eV/ml}$.

rium of reaction Eq. (5) shifts towards the formation of Cl_3^- ions only if the concentration of Cl^- ions in the solution is very high.

Analyzing the kinetics of the appearance of the signal for Cl_3^- at 220 nm it was found that the experimental curves recorded at different absorbed doses for 5 M solutions of NaCl are well described in terms of the simple scheme of reaction (4) and (5). A value of $k_4 = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was derived from the disappearance of the Cl_2^- absorption and introduced into the calculation. The best agreement between experimental data and the simulation was achieved with the rate constants $k_{5b} = 1.1 \times 10^5 \text{ s}^{-1}$ and $k_{5f} = 2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and an extinction coefficient for the Cl_2^- of $\epsilon_{220} = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The equilibrium constant for reaction (5) $K_5 = k_{5f}/k_{5b}$ determined by this optimization calculation is found to be 0.18 M^{-1} , *i.e.* it is in full agreement with the value measured previously [21]. Thus, the results of our studies show that the interaction of two Cl_2^- ions yields most likely a Cl_2 molecule.

The effect of Br^- ions

It was observed that even minor amounts ($\geq 10^{-6} \text{ M}$) of Br^- ions in concentrated solutions of NaCl (1–5 M) change substantially the absorption in the far UV region. A new intense

absorption band appears with a maximum at 230 nm. Fig. 3b illustrates this process for a 1 M solution of NaCl containing 10^{-5} M of NaBr. It can be seen that vanishing of the absorption band at 340 nm, corresponding to the Cl_2^- radical anions, is accompanied by the appearance of an intense band with a maximum at 230 nm.

With up to 10^{-3} M Br^- ions present, the Cl_2^- radical anions formed initially ($\lambda_{\text{max}} = 340$ nm) are rapidly converted into ClBr^- ($\lambda_{\text{max}} = 350$ nm) and Br_2^- ($\lambda_{\text{max}} = 360$ nm) radical anions. As these short-lived radical anions disappear, an absorption with maxima at 230 nm and 245 nm appears in the UV region. Upon a tenfold increase in the concentration of Br^- ions (10^{-2} M NaBr), a signal for the Br_2^- ($\lambda_{\text{max}} = 360$ nm) is observed in the optical spectrum one microsecond after the electron pulse. The disappearance of this specie results finally in a virtually single band with a maximum at 245 nm (Fig. 3c). By analyzing the development of this process in the UV region, one can clearly follow the complex pattern of the chemical transformations involved: first, a band with a maximum at 230 nm appears and, subsequently, it transforms into a band with a maximum at 245 nm.

Finally, in the presence of 0.1 M of NaBr in a 1 M solution of NaCl, as well as in the absence of chlorides in the solution, the Br_2^- generated after an electron pulse disappear to give a product responsible for an intense absorption band with a maximum at 265 nm. This product is known [22, 23] and belongs to the tribromide ion Br_3^- .

The absorption bands with maxima at 230 nm and 245 nm, which appear on pulse irradiation of chloride

solutions containing different amounts of bromide (Figs. 3b and c) can be attributed to the formation of mixed trihalide ions, Cl_2Br^- and ClBr_2^- . In solutions containing either only chlorides or only bromides, Cl_3^- ($\lambda_{\text{max}} = 220$ nm) and Br_3^- ($\lambda_{\text{max}} = 265$ nm), respectively, are generated.

Mixed trihalide ions

The mixed Cl_2Br^- and ClBr_2^- species are known [21] to be formed in the reactions of Cl_2 and ClBr molecules with Cl^- and Br^- ions in acidic aqueous solutions. The species Cl_2Br^- is responsible for an intense band with a maximum at 232 nm in the optical spectrum. Due to this fact, the product that results from the decay of Cl_2^- radical anions in the presence of $\sim 10^{-5}$ M of Br^- ions and that gives rise to the absorption band at 230 ± 2 nm (see Fig. 3b) can be identified as the above mentioned specie. ClBr_2^- ions have an absorption band with a maximum at 245 nm so that we judge that the absorption we observed in our experiments at this wavelength in the presence of Br^- concentrations up to 10^{-2} M is caused by this compound (see Fig. 3c).

We propose the following set of reactions as the pathway to Cl_2Br^- in the radiation-induced chemical oxidation of chloride ions in N_2O -saturated weakly acidic solutions (pH = 3.3). First, this set of reactions includes reactions (4) and (5) considered above with the rate constants found for them. These reactions give rise to the formation of Cl_2 and Cl_3^- . Second, the set was supplemented by the reactions that, in accordance with a previous study [21], allow for the formation of mixed chlorine and bromine compounds in the reactions of Cl_2 molecules with Br^- ions:

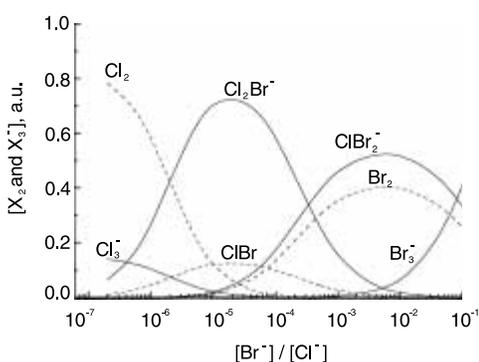


Fig. 4. Calculated dependence of relative concentrations of chlorine-bromine products on the ratio $[\text{Br}^-]/[\text{Cl}^-]$ at $[\text{Cl}^-] = 1$ M.

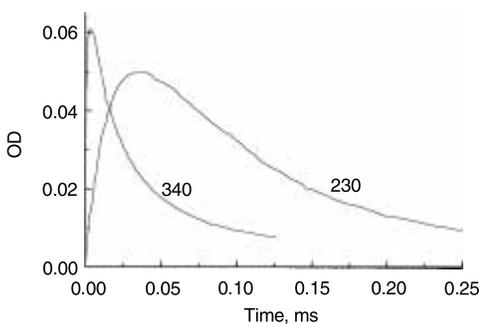


Fig. 5. Decay of Cl_2^- ($\lambda_{\text{max}} = 340$ nm) and the formation and hydrolysis of Cl_2Br^- ($\lambda_{\text{max}} = 230$ nm) at different times after the pulse. Solution: 4 M NaCl, 1×10^{-5} M NaBr, N_2O , pH = 6.8. Pulse duration 20 ns; absorbed dose 6.1×10^{16} eV/ml.

The rate constant for the reaction of Cl_2 with Br^- ions in 1 M HCl (k_{10f}) has been measured using a pulsed-accelerated-flow spectrophotometer (PAF) [21]. The value was found to be $(7.7 \pm 1.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Thus, this is a diffusion-controlled reaction. In our computer simulation the reported values were taken into account, and the best optimization results were attained for $k_{10b} = (6.0 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $K_{10} = k_{10f}/k_{10b} = (6.7 \pm 1.3) \times 10^5 \text{ M}^{-1}$. The ratio of the forward to back reaction rate constants for reaction (11) was derived from the known value $K_{11} = k_{11f}/k_{11b}$, equal to $(6.0 \pm 0.3) \text{ M}^{-1}$ [21]. The best agreement with the experimental results was attained for $k_{11f} = 1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{11b} = 1.7 \times 10^5 \text{ s}^{-1}$ with $K_{11} = 5.9 \text{ M}^{-1}$. The partial transformation of Cl_2Br^- in the reaction with the Br^- ion to give ClBr_2^- ($k_{12} = 3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) was also taken into account (the extinction coefficient of the last-mentioned species at 230 nm is $1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [21]). But it was further assumed that the dissociation reactions of ClBr_2^- to $\text{ClBr} + \text{Br}^-$ and to $\text{Br}_2 + \text{Cl}^-$ are rather slow and do not play a significant role over the time span under interest. The set of reactions proposed accounts for the appearance of an optical absorption at 230 nm in a 1 M solution of NaCl in the

Table 1. Reactions, constants and optical characteristics of trihalide ions.

Reaction	k	K_{eq}, M^{-1}	Optical characteristics of X_3^-		
			X_3^-	λ_{max}, nm	$\epsilon \times 10^{-4} M^{-1} s^{-1}$
$Cl_2 + Cl^- \rightleftharpoons Cl_3^-$	$2.0 \times 10^4 M^{-1} s^{-1}$	0.18	Cl_3^-	220	1.3×10^4
$Cl_3^- \rightleftharpoons Cl_2 + Cl^-$	$1.1 \times 10^5 s^{-1}$				
$Cl_2 + Br^- \rightleftharpoons Cl_2Br^-$	$6.0 \times 10^9 M^{-1} s^{-1}$	6.7×10^5	Cl_2Br^-	230	3.6×10^4
$Cl_2Br^- \rightleftharpoons Cl_2 + Br^-$	$9.0 \times 10^3 s^{-1}$				
$ClBr + Cl^- \rightleftharpoons Cl_2Br^-$	$1.0 \times 10^6 M^{-1} s^{-1}$	6.0	$ClBr_2^-$	245	2.2×10^4
$Cl_2Br^- \rightleftharpoons ClBr + Cl^-$	$1.7 \times 10^5 s^{-1}$				
$Cl_2Br^- + Br^- \rightleftharpoons ClBr_2^- + Cl^-$	$3.0 \times 10^8 M^{-1} s^{-1}$				
$Br_2 + Br^- \rightleftharpoons Br_3^-$	$9.6 \times 10^8 M^{-1} s^{-1}$	17.5	Br_3^-	265	4.4×10^4
$Br_3^- \rightleftharpoons Br_2 + Br^-$	$5.5 \times 10^7 s^{-1}$				

presence of $(1-10) \times 10^{-6} M$ of Br^- ions. The extinction coefficient of Cl_2Br^- calculated by optimization of experimental data proved to be $(3.6 \pm 0.4) \times 10^4 M^{-1} cm^{-1}$. This result is in good agreement with the value found in the study cited [21], $3.3 \times 10^4 M^{-1} cm^{-1}$.

The mechanism of formation of $ClBr_2^-$ (a band with a maximum at 245 nm) in a 1 M solution of NaCl in the presence of $10^{-3}-10^{-2} M$ of Br^- ions is much more intricate because, under these conditions, apart from the Cl_2 molecules, $ClBr$ and Br_2 molecules are also formed (together with Cl_3^- , Cl_2Br^- , and $ClBr_2^-$). This is due to the radiation-induced oxidation of Cl^- and Br^- ions, the formation of Cl_2^- , $ClBr^-$, and Br_2^- and to the establishment of an equilibrium between the above-mentioned species corresponding to definite contents of Cl^- and Br^- in the solution. The uncertainty of the initial yields of the oxidation products of the Cl^- and Br^- ions as well as the reactions between them which take place over the same time span hamper appreciably the optimization of experimental data (the arbitrariness in choosing the optimization parameters becomes too pronounced). Therefore, we rejected the attempt to perform a computer simulation of the radiation-induced chemical formation of the chloride and bromide oxidation products in aqueous solutions at fairly high concentrations of Br^- ions 10^{-3} to $10^{-2} M$. For a Br^- concentration of $10^{-2} M$ (Fig. 3c) the absorption band at 245 nm corresponding to $ClBr_2^-$ obviously predominates in the spectrum, so that we could calculate its extinction coefficient. For this purpose we used the known [21] equilibrium constant for the reaction

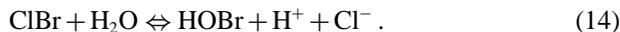


$K_{13} = [Br_2Cl^-]/[Br_2][Cl^-] = 1.3 \pm 0.3 M^{-1}$ and the known extinction coefficient of the Br_2^- , $\epsilon_{360 nm} = 9.9 \times 10^3 M^{-1} cm^{-1}$ [17]. In addition, we took into account the fact that, after the decay of two Br_2^- and establishing an equilibrium (13), the sum of the relative concentrations of Br_2 and Br_2Cl^- is equal to 1. The ϵ value for Br_2Cl^- at 245 nm was found to be $(2.2 \pm 0.3) \times 10^4 M^{-1} cm^{-1}$, which is consistent with the value of $2.5 \times 10^4 M^{-1} cm^{-1}$ measured previously [21].

Thus we found by pulse radiolysis that in the presence of Br^- ions ($\geq 10^{-5} M$), the Cl_2^- resulting from the oxidation of Cl^- ions by OH radicals in weakly acidic 1 M solutions of NaCl saturated with N_2O are transformed into

$ClBr^-$ radical anions, or into Br_2^- in the case of higher Br^- concentrations ($\geq 10^{-3} M$). The results obtained indicate also that recombination of the above-mentioned radical anions and the reactions of the products thus formed with the Cl^- and Br^- ions present in the solution give rise to a broad range of simple and mixed both molecular (Cl_2 , $ClBr$, Br_2) and ionic (Cl_3^- , Cl_2Br^- , $ClBr_2^-$, Br_3^-) products. Table 1 lists the reactions demonstrating their relationship in the presence of Cl^- and Br^- ions and the corresponding equilibrium constants. Fig. 4 shows the relative concentrations of various chlorine- and bromine-containing species depending on the $[Br^-]/[Cl^-]$ ratio. Known [21] equilibrium constants for $ClBr_2^-$ ($K = [ClBr_2^-]/([ClBr^-][Br^-]) = 1.8 \times 10^4 M^{-1}$ and $K_{13} = [ClBr_2^-]/([Br_2][Cl^-]) = 1.3 M^{-1}$) were used in the calculations also. It can be seen that the introduction of Br^- ions induces gradual transformation into mixed halogen-containing compounds, Cl_2Br^- and $ClBr$. For a $[Br^-]/[Cl^-]$ ratio of $5 \times 10^{-6}-1 \times 10^{-4}$, these compounds are the major components, while at values higher than 5×10^{-4} , the predominant species become $ClBr_2^-$ and Br_2 .

We studied the radiation-induced oxidation of concentrated solutions of chlorides in the presence of small admixtures of bromides under specific (model) conditions that ensured almost exclusive formation of OH radicals (by the presence of N_2O) and relatively high stability of the oxidation products formed, e.g. halogen molecules and trihalide ions. The latter point is due to the fact that we used weakly acidic solutions ($5 \times 10^{-4} M$ HCl). When the solution acidity and the chloride concentration decrease, halogen molecules are hydrolyzed. Trihalide ions are hydrolyzed to a markedly lower extent compared to the molecules. Therefore, the channel of hydrolytic decomposition is provided by halogen molecules. According to [21], $ClBr$ is hydrolyzed to give hypobromous acid $HOBr$ as follows:



This could explain why the optical signal at 230 nm which is attributed to Cl_2Br^- vanished at pH 6.8 in the 100 μs time scale as shown in Fig. 5, while it is stable at pH = 3.3. The formation of Cl_2Br^- from Cl_2^- is faster so that its build-up is shown in Fig. 5 in the 10 μs range. Its decay *via* reactions (11) and (14) follows the typical pattern of consecutive reactions with the maximum concentration at about 35 μs

and the point of deflection in the concentration/time curve at double the time.

Conclusion

The results of this study demonstrate an exceptionally important role of even small contents of Br^- ions in the radiation-induced oxidation of Cl^- ions. At an early (radical-ion) stage, the Cl_2^- radical anions are able to be transformed into ClBr^- and Br_2^- radical anions. Their subsequent decay gives rise to a broad range of molecular (Cl_2 , ClBr , Br_2) and ionic (Cl_3^- , Cl_2Br^- , ClBr_2^- , Br_3^-) products, which are equilibrated with one another. If bromide ions are present the further reaction of Cl_2 will also generate bromine containing species (and not Cl_3^-) as the reaction rate constants of reactions (5) and (10f) are more than 5 orders of magnitude apart. In addition to high chloride concentrations, real brines contain bromides whose content can amount to several percent. In this case, as indicated by the results of this study, radiolysis of solutions would give, at the radical step, Cl_2^- , ClBr^- , and Br_2^- radical anions. Recombination of these species with one another gives rise to mixed halogen molecules and trihalide ions (molecular step). Figs. 2 and 4 illustrate the relative proportions of these compounds at equilibrium depending on the content of Br^- ions. In a disposal in salt they all would be involved in reactions with the impurities dissolved in brines or contribute to the corrosion of steel containers and the spent nuclear fuel stored in them. The hydrolysis of mixed halogen molecules results in the formation of hypobromite HOBr . That compound is the starting substance for the formation of more stable bromates of higher oxidation state.

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