Pulse radiolysis study of the oxidation of the I⁻ ions with the radical anions Br₂⁻ in an aqueous solution: formation and properties of the radical anion BrI⁻

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The radiation chemical redox transformations in solutions of bromides in the presence of minor additives of iodides were studied by pulse radiolysis. The change in the concentrations of the Br⁻ and I⁻ ions changes the ratio of the formed short-lived radical anions Br₂⁻⁻, BrI⁻⁻, and I₂⁻⁻. The spectrum of the mixed radical anion BrI⁻⁻ contains a broad optical band at 370 nm with $\varepsilon_{370} = 9650 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$. The reduction potential of the BrI⁻⁻/Br⁻, I⁻ pair is 1.25 V. The rate constants for the forward and backward reactions Br₂⁻⁻ + I⁻ \implies BrI⁻⁻ + Br⁻ are $k_f = 4.3 \cdot 10^9$ and $k_r = 1.0 \cdot 10^5 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$.

Key words: pulse radiolysis, oxidation, reaction, chlorine, bromine, iodine, ions, radicals, kinetics.

The reactions of one-electron oxidation of the Cl⁻, Br⁻, and I⁻ ions that occur upon the radiolysis or photolysis of aqueous solutions of halides afford intermediate short-lived radical anions Cl₂⁻⁻, Br₂⁻⁻, and I₂⁻⁻ (see review¹). They exhibit properties of strong oxidants. The rate constants for many one-electron oxidation reactions of organic and inorganic compounds involving these radical anions were measured by pulse radiolysis and photolysis.²

It was found³ that Cl_2 .⁻ interacts with the Br⁻ ion to form the mixed radical anion ClBr^{.-}. This species occupies an intermediate position between the radical anions Cl_2 ⁻⁻ and Br_2 ⁻⁻ in the properties. For instance, the maximum of the optical band (λ_{max}) in the spectrum of this species lies at a wavelength of 350 nm, and the molar absorption coefficient (ϵ) is 9.3 · 10³ L mol⁻¹ cm⁻¹.³ The corresponding parameters for Cl_2 ⁻⁻ are 340 nm and 8.8 · 10³ L mol⁻¹ cm⁻¹,⁴ and for Br₂⁻⁻ they are 360 nm and 9.9 · 10³ L mol⁻¹ cm⁻¹.⁵ The standard redox potentials of the Cl_2 .⁻/2Cl⁻ and Br_2 .⁻/2Br⁻ pairs are 2.09 and 1.66 V.⁶ The calculated E^0 potential for the ClBr^{-/}/Cl⁻,Br⁻ pair is 1.85 V.³ The radical anions Cl_2 ·- interact with the I⁻ ion in a different manner.⁷ In this case, no mixed radical anion is formed, but the I atoms, which are further transformed into the radical anions I_2 ., are generated. In authors' opinion,⁷ this difference in the mechanism of oxidation of the Br⁻ and I⁻ ions with the radical anions Cl_2 ·- is a consequence of the difference between the values

 $E^{0}(\text{Cl}_{2}^{-}/2\text{Cl}^{-}) = 2.09 \text{ V}$ and $E^{0}(\text{Br}^{-}/\text{Br}^{-}) = 1.93 \text{ V}$, as well as $E^{0}(\text{I}^{-}/\text{I}^{-}) = 1.33 \text{ V}$. In the first case, the potential difference is only 0.16 V, which is favorable for the organization of a mixed orbital in ClBr⁻⁻. In the second case, the difference reaches 0.76 V, and the transfer of an electron from I⁻ to Cl₂⁻⁻ turns out to be energetically more favorable.

A comparison of $E^0(\text{Br}_2 \cdot -/2\text{Br}^-) = 1.66 \text{ V}$ with $E^0(\text{I}_2 \cdot -/2\text{I}^-) = 1.03 \text{ V}$ and $E^0(\text{I}^-/\text{I}^-) = 1.33 \text{ V}$ (see Ref. 6) suggests that the radical anions $\text{Br}_2 \cdot -$ can oxidize the I⁻ ions. However, this reaction was not studied until presently. The potential difference between $E^0(\text{Br}_2 \cdot -/2\text{Br}^-)$ and $E^0(\text{I}^-/\text{I}^-)$ is 0.33 V, and the formation of the mixed radical anions BrI^- can be expected, as it is observed for the reaction of $\text{Cl}_2 \cdot -$ with the Br^- ion.

The study of the redox reactions involving chlorine, bromine, and iodine is important due to their wide abundance in practical activities. For example, when chlorine is used for the disinfection of drinking water, admixtures of bromine and iodine are oxidized with chlorine to form diverse oxide compounds. Bromine and iodine are obtained by the chlorination of hydrochloric brines with the evolution of molecular forms of these halogens. Therefore, the problem of studying the mechanisms and kinetics of the redox reactions involving chlorine, bromine, and iodine is topical. The present work is devoted to the pulse radiolysis study of the reaction of the Br₂⁻⁻ radical anions with the I⁻ ions in an aqueous solution.

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Experimental

A pulse radiolysis technique⁸ and the van de Graaf generator software⁹ were used. The duration of an electron pulse with an energy of 3.8 MeV was varied in the interval from 3 to 20 ns.¹⁰ Optical signals were obtained by averaging the data from ten pulses. The absorbed dose in a pulse was measured from the optical absorption of the hydrated electron in water¹¹ at 700 nm and its molar absorption coefficient at this wavelength equal to $1.9 \cdot 10^4$ L mol⁻¹ cm⁻¹. The radiation chemical yield of electrons in water at pH 7 is 2.6 particles per 100 eV of the absorbed energy.¹²

The salts NaBr and NaI (Merck) were additionally recrystallized. Solutions were prepared using triply distilled water and saturated with nitrous oxide (N_2O).

Results and Discussion

Experiments were carried out with weakly acidic $(5 \cdot 10^{-4} M \text{ HClO}_4)$ aqueous solutions of NaBr containing NaI additives and saturated with N₂O. Upon the radiolysis of these solutions, the hydrated electrons e_{aq}^- , formed in the primary processes along with the 'OH hydroxy radicals, are transformed into the 'OH radicals ([N₂O] = $2.6 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ and $k_1 = 9.1 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$)¹³ due to the reaction

$$e_{aq}^{-} + N_2 O + H_2 O \longrightarrow OH + N_2 + OH^{-}.$$
 (1)

Thus, the presence of N_2O makes it possible to generate predominantly the 'OH radicals by the ionizing irradiation of water. The H⁺ ions catalyze the oxidation of the Br⁻ ions with the 'OH radicals in aqueous solutions.⁵

After an aqueous 0.1 *M* solution of NaBr (pH 3.3) saturated with N₂O was irradiated with a pulse of accelerated electrons, an absorption band of the radical anion Br₂⁻⁻ with a maximum at 360 nm (ε_{Br_2} ⁻⁻ = 9900 L mol⁻¹ cm⁻¹)^{5,14} appeared in the optical spectrum. The disappearance of Br₂⁻⁻ is accompanied by the appearance of a new optical absorption: a band with a maximum at 265 nm induced by the formation of the Br₃⁻⁻ ion due to the reactions

$$Br_2^{-} + Br_2^{-} \implies Br_2 + 2 Br^{-},$$
 (2)

$$Br_2 + Br^- \Longrightarrow Br_3^-. \tag{3}$$

We considered the mechanism of this process in detail.¹⁴ The rate constant for forward reaction (2) was determined as $k_f = 3.0 \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, and the rate constants for the forward and backward reactions (3) were also calculated.

In the present study, we found that the addition of $5 \cdot 10^{-6}$ *M* NaI to an 0.1 *M* solution of NaBr (pH 3.3) saturated with N₂O resulted in noticeable changes in the optical spectrum. As can be seen from the data in Fig. 1, in this case, the disappearance of the absorption of the radical anion Br₂⁻⁻ at 360 nm is accompanied by the appearance of the band with a maximum at 258 nm instead of the band



Fig. 1. Absorption spectra of a 0.1 *M* solution of NaBr with pH 3.3 containing $5 \cdot 10^{-6} M$ NaI and saturated with N₂O 0.7 (*I*), 10 (2), 32 (3), and 250 µs (4) after an electron pulse. The pulse duration is 40 ns, and the absorbed dose is 15 Gy and corresponds to the formation of the 'OH radicals at a concentration of 8.6 $\cdot 10^{-6}$ mol L⁻¹.

at 265 nm, as it was observed in the solution without I⁻ ions. In addition, the band intensity is approximately twice as large. The increase in the absorption intensity at 258 nm is accompanied by the clearing up of the solution at the wavelength 225 nm corresponding to the absorption band of the I⁻ ions ($\lambda_{max} = 225$ nm, $\epsilon = 1.1 \cdot 10^4$ L mol⁻¹ cm⁻¹).¹⁵ This is induced, most probably, by the formation, along with the Br₃⁻ ion, of the mixed trihalide ion Br₂I⁻ in the reaction

$$Br_2 + I^- \Longrightarrow Br_2 I^-. \tag{4}$$

Simple and mixed trihalide ions appear in reactions of molecular halogens with halogen ions. According to earlier published data,¹⁶ the spectrum of Br_2I^- has an absorption band with a maximum at 253 nm and its ε is $5.5 \cdot 10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$, and Br_3^- absorbs at 266 nm with $\varepsilon = 4.1 \cdot 10^4 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$.¹⁷ Under the conditions of our experiments, we observed, most likely, a mixture of two types of the indicated trihalide ions, whose concentration ratio corresponds to the ratio of the bromide and iodide ions present in the solution.

The absorption spectra of a 0.1 *M* solution of NaBr (pH 3.3) saturated with N₂O and containing a higher concentration of the I⁻ ions $(5 \cdot 10^{-6} M \text{ NaI})$ are shown in Fig. 2. 0.3 µs after an accelerated electron pulse with a duration of 5 ns, the optical spectrum contains an absorption band with a maximum at 360 nm due to the radical anion Br₂⁻⁻. The high concentration of the Br⁻ ions provided the nearly complete capture of the 'OH radicals, formed by water radiolysis, with these ions rather than with I⁻. Using the absorbance value and the known⁵ value $\varepsilon = 9.9 \cdot 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, one can determine the concentration of the formed radical anions Br₂⁻⁻, which is $8.6 \cdot 10^{-7} \text{ mol L}^{-1}$ for a solution containing 0.1 *M* NaBr. For this concentration of the radical anions, their interaction with the I⁻ ions prevails, most likely, over their re-

combination according to the second-order law. In fact, the data in Fig. 2 show that after a pulse the absorption band maximum shifts with time toward long wavelengths, reaching its position at ~370 nm. It is important that the changes observed in an optical region of 300-400 nm are accompanied by the noticeable clearing up of the solution at 225 nm (Fig. 3). This clearing up is caused by the disappearance of the free I⁻ ions. It seems natural to attribute these facts to the interaction of the radical anions Br_2 . with the I⁻ ions. This reaction is rather fast and, as can be seen in Fig. 2, in the presence of $5 \cdot 10^{-5} M$ NaI the reaction ceases $\sim 3 \mu s$ after an electron pulse. At long times $(\sim 500 \,\mu\text{s}, \text{when pulses with a duration of 5 ns are used})$, the optical absorption shown in Fig. 2 decreases without appreciable changes in the band shape. The decay kinetics is described by the second-order kinetic equation, and $\tau_{1/2}$ decreases proportionally with an increase in the absorbed dose in a pulse. Reactions (2)—(4) result in the appearance of an absorption band in the spectrum with a maximum at 253 nm belonging to the Br_2I^- ion.

In a 0.1 *M* solution of NaBr containing $5 \cdot 10^{-4}$ *M* NaI and more, already 1 µs after an accelerated electron pulse the primarily appeared absorption band of the radical anion Br₂^{•-} at 360 nm is transformed into an absorption band at 385 nm. The latter is due to the radical anion I₂^{•-}.¹⁸⁻²⁰ It can be concluded that the interaction of the radical anions through the step of formation of the mixed product ceases by the formation of the I₂^{•-} species.

It is known^{3,5} that the radical anion Br_2 ⁻⁻ has a weak absorption at 650–750 nm ($\varepsilon_{700} = 400-600 \text{ L mol}^{-1} \text{ cm}^{-1}$). The kinetic curves for the appearance of an optical absorption at a wavelength of 725 nm in a 0.1 *M* solution of NaBr containing 5 · 10⁻⁵ *M* NaI are shown in Fig. 4. In the presence of the I⁻ ions, the weak absorption at the wave-



Fig. 2. Absorption spectra of a 0.1 *M* solution of NaBr with pH 3.3 containing $5 \cdot 10^{-5} M$ NaI and saturated with N₂O 0.3 (*I*), 1.5 (*2*), 3.0 (*3*), and 6.0 µs (*4*) after an electron pulse. The pulse duration is 5 ns, and the absorbed dose is 1.6 Gy and corresponds to the formation of the 'OH radicals in a concentration of 9.3 $\cdot 10^{-7}$ mol L⁻¹.



Fig. 3. Kinetic curve of the change in the absorption at 225 nm. The pulse duration is 10 ns, and the absorbed dose is 3.5 Gy; the data are presented for the same solution as in Fig. 2.

length 725 nm caused by the radical anions Br_2^{--} continues to increase within several microseconds after the end of an electron pulse. Note that the I_2^{--} radical anions give a more intense (by ~3 times) absorption at the indicated wavelength ($\varepsilon_{725} = 3 \cdot 10^3$ L mol⁻¹ cm⁻¹).^{7,8,20} The absorption at 725 nm increases substantially with an increase in the content of the I⁻ ions in a solution ($5 \cdot 10^{-4}$ *M* NaI and more), and this correlates with the transformation of the radical anions Br_2^{--} into I_2^{--} observed at wavelengths of 360-385 nm.

The experimental facts indicate that the radical anion $Br_2^{\cdot-}$ oxidizes the I⁻ ions. Along with the radical anion $I_2^{\cdot-}$, which is formed at rather high content of the I⁻ ions in the solution (> 5 \cdot 10⁻⁴ *M* NaI), at a lower concentration of the I⁻ ions this reaction also affords another



Fig. 4. Kinetic curve of the change in the absorption at 725 nm. The pulse duration is 10 ns, and the absorbed dose is 1.8 Gy; the data are presented for the same solution as in Fig. 2. The smooth line is the calculation by the scheme (see Table 1). The following values were used for $Br_2^{-,}$, $BrI^{-,}$, and $I_2^{-,}$, respectively: $\varepsilon = 560$, 1700, and 2600 L mol⁻¹ cm⁻¹.

species. Its optical characteristics in the UV region resemble those of $Br_2^{\cdot-}$ and $I_2^{\cdot-}$. So, the maximum of its absorption band lies at ~370 nm and the ε value does not substantially differ from ε for the mentioned radical anions. Thus, an increase in the concentration of the I⁻ ions in the solution results in a decrease in the relative content of the unknown intermediate species and, to the contrary, the content of I_2^- increases.

We believe that the interaction of the radical anions $Br_2^{\cdot-}$ with I⁻ produces, in addition to $I_2^{\cdot-}$, the mixed radical anion $BrI^{\cdot-}$. Similar species, namely, the radical anions $CISCN^{\cdot-}$ and $BrSCN^{\cdot-}$, were found by pulse radiolysis upon the oxidation of chloride²¹ and bromide²² in the presence of minor additives of the SCN^- ions. The formation of the mixed radical anion $CIBr^{\cdot-}$ has recently been observed by pulse radiolysis during the oxidation of the Br^- ions with the radical anions $Cl_2^{\cdot-}$ in a 1 *M* solution of NaCl containing an admixture of the Br^- ions (less than $10^{-3} \text{ mol } L^{-1}$). It is most likely that the radical anions $Br_2^{\cdot-}$ interact with the I⁻ ions *via* an analogous mechanism due to the following consecutive reactions

$$Br_2^{-} + I^{-} \Longrightarrow BrI^{-} + Br^{-}, \tag{5}$$

$$BrI^{-} + I^{-} \Longrightarrow I_{2}^{-} + Br^{-}.$$
(6)

The ratio of the radical anions Br_2 ., BrI., and I_2 . formed upon the radiation chemical oxidation of the $Br^$ and I^- ions is determined by the concentrations of the halogen ions present in the solution.

The computer simulation of the process was performed to describe the oxidation of the I⁻ ions with the radical anions Br_2 . in the solutions under study. The interaction of the Cl⁻ atom with the Cl⁻ ion affording the radical anion Cl_2 .⁻ and the analogous reaction for bromine proceed with very high rate constants: $1.0 \cdot 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (see Ref. 5) and $1.1 \cdot 10^{10}$ L mol⁻¹ s⁻¹, respectively.^{18,19} We accepted that the rate constant for the similar reaction between the I \cdot atom and the Br- ion affording the radical anion BrI^{$\cdot-$} is 1.0 \cdot 10¹⁰ L mol⁻¹ s⁻¹. The rate constant for the reaction between the H atom and the radical anion Br_2 .⁻ is unknown. We accepted that it is equal to $7 \cdot 10^9 \text{ Lmol}^{-1} \text{ s}^{-1}$, measured²³ for an analogous reaction of the H atom with the radical anion Cl_2 . We obtained the rate constant values for other unknown reactions in the reaction scheme (Table 1) by the simulation of the kinetics of the change in the optical absorption in the studied solutions at different wavelengths. The changes in the absorption at 300-400 nm and 725 nm reflect the formation, transformation, and decay of the radical anions Br₂⁻⁻, BrI⁻⁻, and I_2 ., and the change at 225 nm shows the disappearance of the I- ions in these reactions. The recombination rate constant of the radical anion BrI⁻⁻ was selected on the basis of the known values for similar reactions of the

 $Br_2^{\cdot-}$ and $I_2^{\cdot-}$ radical anions. The following values were accepted for the initial yields of the products of water radiolysis¹²: $G(e_{aq}^{-}) = 2.7$, $G(H^{\cdot}) = 0.6$, and $G(OH^{\cdot}) = 2.8$. The presence of 0.1 M NaBr or other halides exerts no substantial effect²⁵ on the initial yields of the water radiolvsis products. It was also taken into account that the hydrated electrons formed in reaction (1) are transformed into the hydroxy radicals. It is found that the use of the indicated scheme allows the satisfactory simulation to be performed for the kinetics of the change in the optical absorption, generated by an electron pulse, at all wavelengths. In this case, the known molar absorption coefficients of the radical anions $Br_2^{\cdot-}$ and $I_2^{\cdot-}$ and the I^- ions involved in the reactions and the $\epsilon_{IBr,-}$ value chosen for consistency were used for each wavelength. Figures 4, 5, a, and 5, b illustrate the agreement between the calculations and the change in the absorption of a 0.1 M solution of NaBr containing $5 \cdot 10^{-5} M$ NaI at 725, 340, and 400 nm, respectively, after an electron pulse 5 ns long. The contributions of the absorption from particular radical anions $Br_2^{\cdot-}$, $BrI^{\cdot-}$, and $I_2^{\cdot-}$ involved in the chemical transformations are also shown in the figures. Similar results were obtained at other wavelengths using solutions with other concentrations of the components and powers of the absorbed dose. It can be concluded that the proposed scheme provides a satisfactory agreement with experiment.

The ε values for BrI⁻⁻ at different wavelengths, which were obtained by the agreement between the experimental data and calculations using the above-indicated scheme, are shown in Fig. 6. The absorption spectrum of BrI⁻⁻, as can be seen, is a broad absorption band with a maximum at 370±3 nm, and ε at this wavelength is 9650±200 L mol⁻¹ cm⁻¹. A broad optical absorption at

Table 1. Rate constants (*k*) for the reactions used in modeling the oxidation kinetics of the I^- ions with the Br_2^- radical anions

Reaction	$k/L \text{ mol}^{-1} \text{ s}^{-1}$	Reference
$Br^- + OH^- \rightarrow Br^-$	$1.1 \cdot 10^{10}$	5
$Br_2^{\cdot -} \rightarrow Br^{\cdot} + Br^{-}$	$4.6 \cdot 10^4 *$	5
$Br^{\cdot} + Br^{-} \rightarrow Br_{2}^{\cdot -}$	$1.0 \cdot 10^{10}$	5
$Br_2 \cdot - + Br_2 \cdot - \rightarrow Br_3 - + Br^-$	$3.4 \cdot 10^9$	3
$H^{\cdot} + Br_{2}^{\cdot} \rightarrow Br^{-} + HBr$	$7.0 \cdot 10^9$	23
$H^{\cdot} + H^{\cdot} \rightarrow H_2$	$7.8 \cdot 10^9$	24
$Br_2^{\cdot -} + I^- \rightarrow \tilde{B}rI^{\cdot -} + Br^-$	$4.3 \cdot 10^9$	This work
$Br\tilde{I}^{-} + Br^{-} \rightarrow Br_{2}^{-} + I^{-}$	$< 1.0 \cdot 10^{5}$	This work
$BrI^{-} \rightarrow Br^{-} + I^{-}$	$5.7 \cdot 10^8 *$	This work
$Br^- + I^- \rightarrow BrI^{}$	$1.0 \cdot 10^{10}$	This work
$BrI^{-+}I^{-} \rightarrow I_{2}^{} + Br^{-}$	$5.8 \cdot 10^9$	This work
$I_2^{\cdot -} + Br^- \rightarrow \tilde{B}rI^{\cdot -} + I^-$	$4.3 \cdot 10^{6}$	This work
$\tilde{I_2}^{-} \rightarrow I^- + I^-$	$1.1 \cdot 10^{5*}$	18, 19
$\tilde{I^-} + I^* \rightarrow I_2^-$	$1.2 \cdot 10^{10}$	18, 19
$BrI^{-} + Br\overline{I}^{-} \rightarrow Br_2I^{-} + I^{-}$	$3.0 \cdot 10^9$	This work
$I_2^{\bullet-} + I_2^{\bullet-} \rightarrow I_3^{-} + I^{-}$	$3.0 \cdot 10^9$	18, 19
* In s ⁻¹ .		



Fig. 5. Comparison of the experiment with the computer calculation (smooth line) by the scheme (see Table 1) (the data are presented for the same solution as in Fig. 2); *a*, kinetics of the change in the absorption at 340 nm. The absorbed dose is 1.6 Gy. The following values were used for $Br_2^{\cdot-}$, $BrI^{\cdot-}$, and $I_2^{\cdot-}$, respectively: $\varepsilon = 8100$, 5900, and 3600 L mol⁻¹ cm⁻¹. *b*, Kinetics of the change in the absorption at 400 nm. The absorbed dose is 1.2 Gy. The following values were used for $Br_2^{\cdot-}$, $BrI^{\cdot-}$, and $I_2^{\cdot-}$, respectively: $\varepsilon = 5800$, 7400, and 8700 L mol⁻¹ cm⁻¹.

650–750 nm is also characteristic of BrI⁻⁻, and its ϵ_{725} value was calculated as approximately equal to 580 L mol⁻¹ cm⁻¹. Thus, its optical characteristics are intermediate compared to the optical characteristics of the radical anions Br₂⁻⁻ ($\lambda_{max} = 360$ nm and $\epsilon = 9900$ L mol⁻¹ cm⁻¹) and I₂⁻⁻ ($\lambda_{max} = 385$ nm and $\epsilon = 9400$ L mol⁻¹ cm⁻¹).

The equilibrium constant *K* is equal to the ratio of the rate constants for the forward and backward reactions, *i.e.*, k_f/k_b . The calculated data (see Table 1) show that $K_5 > 4.3 \cdot 10^4$ and $K_6 = 1.3 \cdot 10^3$. The constant of the equilibrium

$$BrI^{-} \Longrightarrow Br^{-} + I^{-}$$
(7)

 K_7 is $5.7 \cdot 10^{-2}$ mol L⁻¹.

The equation $K_8 = K_9/K_5$ is valid for the equilibria

$$BrI^{-} = Br^{+} + I^{-}, \qquad (8)$$

$$Br_2^{-} \Longrightarrow Br^{-} + Br^{-}$$
 (9)



Fig. 6. Optical absorption spectrum of the BrI⁻⁻ radical anion.

From the calculated value $K_5 > 4.3 \cdot 10^4$ and known⁵ $K_9 = 4.6 \cdot 10^{-6}$ mol L⁻¹ we determine $K_8 < 1.1 \cdot 10^{-10}$ mol L⁻¹. A comparison of the K_7 and K_8 values shows that BrI⁻⁻ decomposes exclusively *via* reaction (8). This is quite natural, because upon the decomposition of BrI⁻⁻ an electron preferentially adds to the bromine atom, whose oxidation potential (1.93 V) is higher than that for the iodine atom (1.33 V),⁶ *i.e.*, reaction (8) is thermodynamically unfavorable. An analogous situation is observed for the same reason in the case of another mixed radical anion ClBr⁻⁻, for which the equilibrium constant for the decomposition with the formation of the chlorine atom and bromine ion is $3.8 \cdot 10^{-13}$ mol L⁻¹, whereas that with the formation of the chlorine ion and bromine atom is $8.5 \cdot 10^{-3}$ mol L⁻¹.³

The redox potentials of equilibria (5)—(7) are written as follows: $\Delta E_5^{0} = E^0(\text{Br}_2^{-/2}\text{Br}^-) - E^0(\text{Br}^{-/2}\text{Br}^-,\text{I}^-),$ $\Delta E_6^0 = E^0(\text{BrI}^{-}/\text{Br}^{-},\text{I}^{-}) - E^0(\text{I}_2^{-}/2\text{I}^{-}), \text{ and } \Delta E_7^0 =$ = $\tilde{E}^0(\text{BrI}^{-}/\text{Br}^{-},\text{I}^{-}) - E^0(\text{I}^{-}/\text{I}^{-})$. The ΔE^0 value can be expressed through the equilibrium constant K of the corresponding reaction in the form $\Delta E^0 = 0.059 \cdot \log K$. Using the known values K_5 , K_6 , and K_7 , as well as $E^{0}(\text{Br}_{2}^{-}/2\text{Br}^{-}) = 1.66 \text{ V}, E^{0}(\text{I}_{2}^{-}/2\text{I}^{-}) = 1.03 \text{ V}, \text{ and}$ $E^{0}(I^{-}/I^{-}) = 1.33 \text{ V},^{6}$ we find that the redox potential $E^{0}(BrI^{-}/Br^{-},I^{-})$ is <1.39, 1.22, and 1.26 V for equilibria (5), (6), and (7), respectively. The agreement between these values can be recognized as very good, which indicates in favor of the right choice of the reaction scheme that satisfactorily describes the radiation chemical oxidation of the I⁻ ions in aqueous solutions of NaBr. The $E^0(BrI^{-}/Br^{-},I^{-})$ potential can be accepted as equal to 1.25 ± 0.05 V. In fact, as could be expected, the reduction potential of the ClBr⁻⁻ radical anion is intermediate between the potentials for the Br_2^{-} (1.66 V) and I_2^{-} (1.03 V) radical anions.

The ratio between the equilibrium concentrations of Br_2^{-} , BrI^{-} , and I_2^{-} in the absence of their decay at different ratios of the concentrations of the I⁻ and Br⁻ ions in the solution is shown in Fig. 7.

The results of the present study show that the radical anions Br_2 ⁻⁻ oxidize the I⁻ ions to form the radical anions



Fig. 7. Plots of the ratio of the concentrations of the radical anions $Br_2^{-,-}$, $BrI^{-,-}$, and $I_2^{-,-}$ in solution vs I^-/Br^- value.

BrI^{\cdot} and I₂^{\cdot}. The equilibrium shifts to the predominant formation of I_2 · – with an increase in the I– concentration. These radical anions are highly reactive and short-lived species. The rate constants of their recombination are $\sim 3.0 \cdot 10^9$ L mol⁻¹ s⁻¹ (see Table 1). Their decay results in the formation of a large array of molecular (Br_2, BrI, I_2) and ionic $(Br_3^-, Br_2I^-, BrI_2^-, I_3^-)$ products, which exist at equilibrium with each other. The mixed trihalide ions give intense absorption bands in the UV region: for Br₂I- $\lambda_{max} = 253$ nm, $\epsilon = 5.5 \cdot 10^4$ L mol^{-1} cm^{-1} and for $Br \bar{I}_2^{-1}$ $\lambda_{\text{max}}^{\text{max}} = 273 \text{ nm}, \varepsilon = 6.1 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.¹⁶ These anions are formed after the disappearance of the radical anions, and their absorption bands are overlapped with those of Br_3^- ($\lambda_{max}=266$ nm, $\epsilon=4.1\cdot 10^4$ L mol $^{-1}$ cm $^{-1}$) and I^- ($\lambda_{max}=225$ nm, $\epsilon=1.1\cdot 10^4$ L mol $^{-1}$ cm $^{-1}$). ^{16,17} This fact substantially impedes the rigid kinetic analysis of the process of their formation. However, this problem was not stated in our investigation, because the properties of these spacies were studied in detail elsewhere $^{15-17}$. They were produced in the reactions of molecular halogens with halide ions. Nevertheless, at the concentration of the I⁻ ion about $5 \cdot 10^{-6}$ mol L⁻¹ in a 0.1 *M* solution of NaBr, when the formation of the Br3- and Br2I- species prevailed (see Fig. 1), we calculated the rate constant for reaction (1) equal to $2 \cdot 10^{10}$ L mol⁻¹ s⁻¹.

Thus, the radical anions $Br_2^{\cdot-}$ oxidize the I⁻ ions to form the intermediate mixed radical anion $BrI^{\cdot-}$. The reaction between $Cl_2^{\cdot-}$ and the Br^- ion proceeds similarly to form $ClBr^{\cdot-}$. At the same time, $Cl_2^{\cdot-}$ interacts with the I⁻ ion to form the I^{*} atoms, which are further transformed into the radical anions $I_2^{\cdot-.7}$ The potential differences of the pairs $E^0(Br_2^{\cdot-}/2Br^-) = 1.66$ V and $E^0(I^{\cdot}/I^-) = 1.33$ V, as well as $E^0(Cl_2^{\cdot-}/2Cl^-) = 2.09$ V and $E^0(Br^{\cdot}/Br^-) =$ = 1.93 V, are 0.33 and 0.16 V, respectively. A slight difference between the potentials is favorable for the organization of a mixed orbital in BrI⁻⁻ and in ClBr⁻⁻. The difference in the potential values $E^0(\text{Cl}_2^{--}/2\text{Cl}^{--}) = 2.09$ V and $E^0(I^{-}/I^{--}) = 1.33$ V is 0.76 V, and the electron transfer from I⁻ to Cl₂⁻⁻ turns out to be energetically more favorable.

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