Pulse radiolysis study of I⁻ oxidation with radical anions Cl₂•– in an aqueous solution

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Radiation-chemical transformations of chloride solutions in the presence of iodide additives were studied by pulse radiolysis. Radical anion Cl₂•– oxidize I⁻ ion, while in the secondary reactions Cl₂ reacts with I⁻ to form a mixed trihalide ion ICl₂–. A reaction model that satisfactorily describes the experimental data was proposed.

Key words: pulse radiolysis, redox reactions, halides, chlorine, iodine, ions, radicals, kinetics, reaction mechanism, reaction rate constants.

Radiation-chemical or photochemical oxidation of ions Cl–, Br–, and I– in aqueous solutions gives rise to radical anions Cl₂•–, Br₂•–, and I₂•–, respectively.¹ These species have properties of rather strong oxidizing agents. Rate constants of many one-electron oxidation reactions of organic and inorganic compounds involving these radical anions were measured² using pulse radiolysis and photolysis techniques.

It has recently been found³ that Cl₂•– reacts with the Br⁻ ion to form a mixed radical anion ClBr •–. This species is intermediate by its properties between the radical anions Cl₂•– and Br₂•–. For instance, the absorption band maximum (λmax) in its spectrum lies at 350 nm, and the molar absorption coefficient (ε) is 9.3 •10³ L mol⁻¹ cm⁻¹.³ The corresponding parameters for Cl₂•– are 340 nm and 8.8 •10³ L mol⁻¹ cm⁻¹,¹ and those for Br₂•– are 360 nm and 9.9 •10³ L mol⁻¹ cm⁻¹.⁵ The standard redox potentials (E°) for the Cl₂•–/2Cl⁻ and Br₂•–/2Br⁻ pairs are 2.09 and 1.66 V, respectively.⁶ The potential of the ClBr •–/Cl⁻, Br⁻ pair is 1.85 V.³ A comparison of E°(Cl₂•–/2Cl⁻) with E°(I₂•–/2I⁻) = 1.03 V and E°(I•/I–) = 1.33 V⁶ suggests that the radical anions Cl₂•– can oxidize the I⁻ ions. However, this reaction remained unstudied to date. It was of interest to reveal whether the ability of chlorine to form a mixed radical anion ClI•– with iodine is retained, as for bromine, or an increase in the difference of oxidation potentials of chlorine and iodine compared to that of chlorine and bromine would change the reaction character. In addition to scientific reasons, practical problems stimulate the study of this important reactions. Redox reactions involving chlorine, bromine, and iodine are widely abundant in the nature and practical human activities. For example, water decontamination by chlorination remains to be the main process for preparation of drinking water. Technological processes using halogens are widely used in industry. Taking into account the aforesaid, we continue to study the kinetics and mechanism of redox reactions involving halide ions. In this work we studied the pulse radiolysis of reaction of the radical anions Cl₂•– with the I⁻ ions in an aqueous solution.

Experimental

A pulse radiolysis technique⁷ and a software⁸ for the Van de Graaf accelerator have been described earlier. The pulse duration of electrons with an energy of 3.8 MeV was varied from 3 to 20 ns.⁹ Optical signals were obtained by the averaging of data of ~10 pulses. The absorbed dose in a pulse was calculated from the optical absorbance of a hydrated electron in water and ε = 1.9 •10⁴ L mol⁻¹ cm⁻¹. The radiation-chemical yield of hydrated electrons in water at pH 7 after the reaction completion was accepted to be 2.6 species per 100 eV of absorbed energy.¹¹ Concentrated solutions of NaCl were used. Therefore, the salt (suprapur, Merck) was additionally recrystallized. The NaI salt (Merck) was used as received. Solutions were prepared in triply distilled water and saturated with N₂O.

Results and Discussion

Weakly acidic solutions of NaCl (5 •10⁻⁴ M HCl) containing NaI additives were studied. The solutions were saturated with N₂O. Hydrated electrons eaq– formed in
the primary processes of radiolysis of these solution along with hydroxyl radicals OH\(^+\) by the reaction
\[
\text{e}_\text{aq}^- + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{N}_2 + \text{OH}^- (1)
\]
transform into radicals OH\(^+\) ([N\(_2\)O] = 2.6 \cdot 10^{-2} \text{ mol L}^{-1}, k_1 = 9.1 \cdot 10^9 \text{ L mol}^{-1} \text{s}^{-1}).\(^{12}\) Therefore, the presence of N\(_2\)O makes it possible to generate predominantly the OH\(^+\) radicals under water treatment with ionizing radiation. The H\(^+\) ions catalyze the oxidation of the Cl\(^-\) ions with the OH\(^+\) radicals in aqueous solutions.\(^1\)

The absorption spectra of a 1 M solution of NaCl (pH 3.3) saturated with N\(_2\)O and containing NaI (5 \cdot 10^{-5} \text{ mol L}^{-1}) after accelerated electron pulse with a duration of 10 ns are shown in Fig. 1. The high concentration of Cl\(^-\) ions provides the almost complete capture of the OH\(^+\) radicals formed by water radiolysis by these ions rather than by the I\(^-\) ions. The characteristic absorption spectrum of the Cl\(_2\)\(^-\) radical anion with a maximum at 340 nm is observed 0.7 \mu s after a pulse. The concentration of the formed radical anions Cl\(_2\)\(^-\) can be determined from the absorbance using the known value \(\varepsilon = 8.8 \cdot 10^3 \text{ L mol}^{-1} \text{cm}^{-1}\).\(^4\) \([\text{Cl} _2\text{\(^-\)}] = 1.4 \cdot 10^{-6} \text{ mol L}^{-1}\). The data in Fig. 1 show that the intensity of the absorption band of Cl\(_2\)\(^-\) at 340 nm decreases with time, and simultaneously the intensity of an absorption band appeared at 380 nm and caused by the radical anion I\(_2\)\(^-\) increases. The disappearance of Cl\(_2\)\(^-\) is also accompanied by a decrease in the absorption of the solution at \(\lambda = 225 \text{ nm}\) corresponding to the absorption band of the I\(^-\) ions (\(\lambda_{\text{max}} = 225 \text{ nm}, \varepsilon = 1.1 \cdot 10^4 \text{ L mol}^{-1} \text{cm}^{-1}\)).\(^{13}\) The Cl\(_2\)\(^-\) radical anions and I\(^-\) ions decay via the pseudo-first-order reaction. It is reasonable to relate these facts to the oxidation of the I\(^-\) ion with the Cl\(_2\)\(^-\) radical anion followed by the formation of radical anion I\(_2\)\(^-\). The formation of the latter is especially pronounced at \(\lambda = 725 \text{ nm}\), where its absorption is not impeded by the absorption of other short-lived species.\(^{10}\) The kinetics of an increase in the absorbance contributed by the I\(_2\)\(^-\) radical anions at this wavelength for different absorbed doses is shown in Fig. 2. The appearance of the I\(_2\)\(^-\) absorption at \(\lambda = 725 \text{ nm}\) is preceded by the appearance and fast disappearance of the absorption of hydrated electrons at this wavelength. It is seen that the absorption (concentration) of the I\(_2\)\(^-\) radical anion increases with an increase in the absorbed dose. However, the increase in the limiting concentrations is not proportional to the absorbed doses because of the increasing contribution from the secondary reactions of I\(_2\)\(^-\) decay due to its recombination at high doses.

An increase in the concentration of the I\(^-\) ion accelerates the transformation of the Cl\(_2\)\(^-\) radical anion due to the reaction with I\(^-\) to form radical anion I\(_3\)\(^-\). The appearance of the absorption of I\(_2\)\(^-\) at \(\lambda = 380 \text{ nm}\) at different concentrations of the I\(^-\) ion and the same absorbed dose is illustrated in Fig. 3. It is seen that the time of Cl\(_2\)\(^-\) transformation into I\(_2\)\(^-\) shortens with an increase in the I\(^-\) concentration, while the contribution of this process increases compared to the contribution of Cl\(_2\)\(^-\) decay due to recombination.

The recombination of the Cl\(_2\)\(^-\) and I\(_2\)\(^-\) radical anions produces ions Cl\(_3\)^- and I\(_3\)^-, which are equilibrated with molecular chlorine and iodine in solutions of chlorides and iodides, respectively.\(^1\) As found for mixed solutions of chlorides and iodides in the presence of molecular halogen, mixed trihalide ion ICl\(_3\)^- (\(\lambda_{\text{max}} = 225 \text{ nm}, \varepsilon = 4.75 \cdot 10^4 \text{ L mol}^{-1} \text{cm}^{-1}\), \(K_\text{eq} = 6.0 \cdot 10^3 \text{ mol L}^{-1}\)) and I\(_5\)Cl\(^-\) (\(\lambda_{\text{max}} = 225 \text{ nm}, \varepsilon = 4.75 \cdot 10^4 \text{ L mol}^{-1} \text{cm}^{-1}\), \(K_\text{eq} = 0.6 \text{ mol L}^{-1}\))\(^{15}\) can be formed in addition to Cl\(_3\)^- (\(\lambda_{\text{max}} = 220 \text{ nm}, \varepsilon = 1.0 \cdot 10^4 \text{ L mol}^{-1} \text{cm}^{-1}\), \(K_\text{eq} = 5.5 \text{ mol L}^{-1}\))\(^1\) and I\(_5\)\(^-\) (\(\lambda_{\text{max}} = 285 \text{ and } 355 \text{ nm}, \varepsilon = 4.0 \cdot 10^4 \text{ and } 2.6 \cdot 10^4 \text{ L mol}^{-1} \text{cm}^{-1}\), respectively, \(K_\text{eq} = 1.35 \cdot 10^{-3} \text{ mol L}^{-1}\)). The ratio of concentrations of the formed trihalide ions of different types and equilibrated molecular halogen is de-