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Pulse radiolysis study of I^- oxidation with radical anions $Cl_2{}^{\bullet -}$ 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 $Cl_2{}^{\bullet -}$ oxidize I^- ion, while in the secondary reactions Cl_2 reacts with I^- to form a mixed trihalide ion $ICl_2{}^-$. 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 $Cl_2{}^{\bullet -}$, $Br_2{}^{\bullet -}$, and $I_2{}^{\bullet -}$, 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 measured[2] using pulse radiolysis and photolysis techniques.

It has recently been found[3] that $Cl_2{}^{\bullet -}$ reacts with the Br^- ion to form a mixed radical anion $ClBr^{\bullet -}$. This species is intermediate by its properties between the radical anions $Cl_2{}^{\bullet -}$ and $Br_2{}^{\bullet -}$. For instance, the absorption band maximum (λ_{max}) in its spectrum lies at 350 nm, and the molar absorption coefficient (ε) is $9.3 \cdot 10^3$ L mol^{-1} cm^{-1}.[3] The corresponding parameters for $Cl_2{}^{\bullet -}$ are 340 nm and $8.8 \cdot 10^3$ L mol^{-1} cm^{-1},[4] and those for $Br_2{}^{\bullet -}$ are 360 nm and $9.9 \cdot 10^3$ L mol^{-1} cm^{-1}.[5] The standard redox potentials ($E°$) for the $Cl_2{}^{\bullet -}/2\ Cl^-$ and $Br_2{}^{\bullet -}/2\ Br^-$ pairs are 2.09 and 1.66 V, respectively.[6] The potential of the $ClBr^{\bullet -}/Cl^{\bullet}$, Br^- pair is 1.85 V.[3] A comparison of $E°(Cl_2{}^{\bullet -}/2\ Cl^-)$ with $E°(I_2{}^{\bullet -}/2\ I^-) = 1.03$ V and $E°(I^{\bullet}/I^-) = 1.33$ V[6] suggests that the radical anions $Cl_2{}^{\bullet -}$ 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 $ClI^{\bullet -}$ 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 $Cl_2{}^{\bullet -}$ with the I^- ions in an aqueous solution.

Experimental

A pulse radiolysis technique[7] and a software[8] 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[10] at 700 nm and $\varepsilon = 1.9 \cdot 10^4$ 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 N_2O.

Results and Discussion

Weakly acidic solutions of NaCl ($5 \cdot 10^{-4}$ *M* HCl) containing NaI additives were studied. The solutions were saturated with N_2O. Hydrated electrons $e_{aq}{}^-$ formed in

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the primary processes of radiolysis of these solution along with hydroxyl radicals $OH^\bullet$ by the reaction

$$e_{aq}^- + N_2O + H_2O \longrightarrow OH^\bullet + N_2 + OH^- \qquad (1)$$

transform into radicals $OH^\bullet$ ($[N_2O] = 2.6 \cdot 10^{-2}$ mol L^{-1}, $k_1 = 9.1 \cdot 10^9$ L mol^{-1} s^{-1}).[12] Therefore, the presence of N_2O makes it possible to generate predominantly the $OH^\bullet$ radicals under water treatment with ionizing radiation. The H^+ ions catalyze the oxidation of the Cl^- ions with the $OH^\bullet$ radicals in aqueous solutions.[1]

The absorption spectra of a 1 *M* solution of NaCl (pH 3.3) saturated with N_2O and containing NaI ($5 \cdot 10^{-5}$ 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 $OH^\bullet$ radicals formed by water radiolysis by these ions rather than by the I^- ions. The characteristic absorption spectrum of the $Cl_2^{\bullet -}$ radical anion with a maximum at 340 nm is observed 0.7 μs after a pulse. The concentration of the formed radical anions $Cl_2^{\bullet -}$ can be determined from the absorbance using the known value $\varepsilon = 8.8 \cdot 10^3$ L mol^{-1} cm^{-1} [4]: $[Cl_2^{\bullet -}] = 1.4 \cdot 10^{-6}$ mol L^{-1}. The data in Fig. 1 show that the intensity of the absorption band of $Cl_2^{\bullet -}$ at 340 nm decreases with time, and simultaneously the intensity of an absorption band appeared at 380 nm and caused by the radical anion $I_2^{\bullet -}$ increases. The disappearance of $Cl_2^{\bullet -}$ is also accompanied by a decrease in the absorption of the solution at $\lambda = 225$ nm corresponding to the absorption band of the I^- ions ($\lambda_{max} = 225$ nm, $\varepsilon = 1.1 \cdot 10^4$ L mol^{-1} cm^{-1}).[13] The $Cl_2^{\bullet -}$ 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 $Cl_2^{\bullet -}$ radical anion followed by the formation of radical anion $I_2^{\bullet -}$. The formation of the latter is especially pronounced at $\lambda = 725$ 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 $I_2^{\bullet -}$ radical anions at this wavelength for different absorbed doses is shown in Fig. 2. The appearance of the $I_2^{\bullet -}$ absorption at $\lambda = 725$ 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 $I_2^{\bullet -}$ 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 $I_2^{\bullet -}$ decay due to its recombination at high doses.

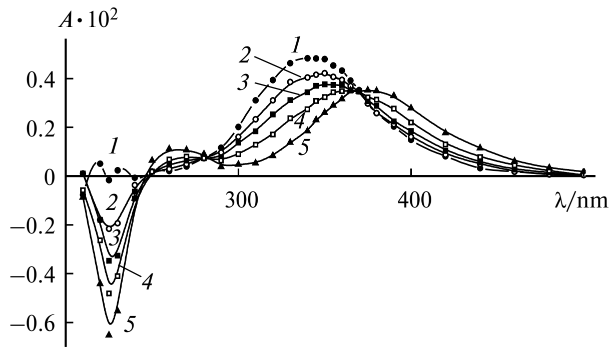

Fig. 1. Absorption spectra of a 1 *M* solution of NaCl (pH 3.3) containing NaI ($5 \cdot 10^{-5}$ mol L^{-1}) and saturated with N_2O 0.7 (*1*), 2.0 (*2*), 3.0 (*3*), 5.0 (*4*), and 12.5 μs (*5*) after electron pulse (pulse duration 10 ns, absorbed dose 6.7 Gy, which corresponds to the formation of $1.8 \cdot 10^{-6}$ mol L^{-1} hydrated electrons).

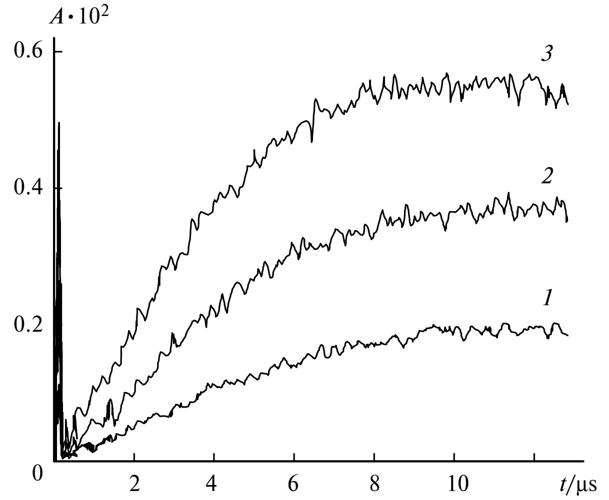

Fig. 2. Kinetic curves of the absorbance change at $\lambda = 725$ nm for different absorbed doses: 6.6 (*1*), 15.2 (*2*), and 28.5 Gy (*3*). For the solution composition, see Fig. 1.

An increase in the concentration of the I^- ion accelerates the transformation of the $Cl_2^{\bullet -}$ radical anion due to the reaction with I^- to form radical anion $I_2^{\bullet -}$. The appearance of the absorption of $I_2^{\bullet -}$ at $\lambda = 380$ 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 $Cl_2^{\bullet -}$ transformation into $I_2^{\bullet -}$ shortens with an increase in the I^- concentration, while the contribution of this process increases compared to the contribution of $Cl_2^{\bullet -}$ decay due to recombination.

The recombination of the $Cl_2^{\bullet -}$ and $I_2^{\bullet -}$ 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 halogens, mixed trihalide ion ICl_2^- ($\lambda_{max} = 225$ nm, $\varepsilon = 4.75 \cdot 10^4$ L mol^{-1} cm^{-1}, $K_{eq} = 6.0 \cdot 10^{-3}$ mol L^{-1}) and I_2Cl^- ($\lambda_{max} = 225$ nm, $\varepsilon = 4.75 \cdot 10^4$ L mol^{-1} cm^{-1}, $K_{eq} = 0.6$ mol L^{-1})[13] can be formed in addition to Cl_3^- ($\lambda_{max} = 220$ nm, $\varepsilon = 1.0 \cdot 10^4$ L mol^{-1} cm^{-1}, $K_{eq} = 5.5$ mol L^{-1})[1] and I_3^- ($\lambda_{max} = 285$ and 355 nm, $\varepsilon = 4.0 \cdot 10^4$ and $2.6 \cdot 10^4$ L mol^{-1} cm^{-1}, respectively, $K_{eq} = 1.35 \cdot 10^{-3}$ mol L^{-1}). The ratio of concentrations of the formed trihalide ions of different types and equilibrated molecular halogens is de-

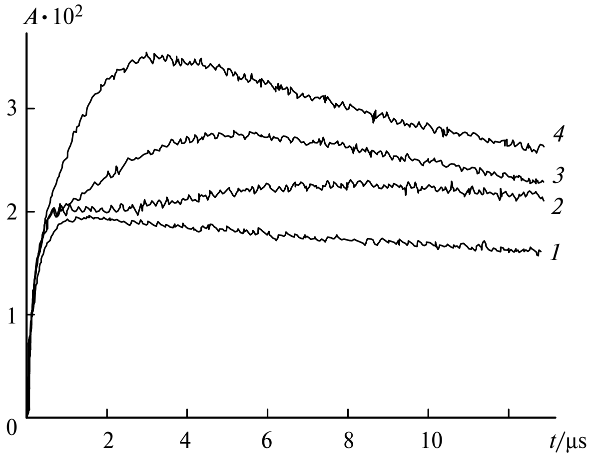

Fig. 3. Kinetic curves of the absorbance change at $\lambda = 380$ nm for different concentrations of NaI: 0 (*1*), $5\cdot10^{-5}$ (*2*), $1\cdot10^{-4}$ (*3*), and $2\cdot10^{-4}$ mol L^{-1} (*4*) (1 *M* solution of NaCl, pH 3.3, saturated with N_2O; pulse duration 10 ns, absorbed dose 20 Gy).

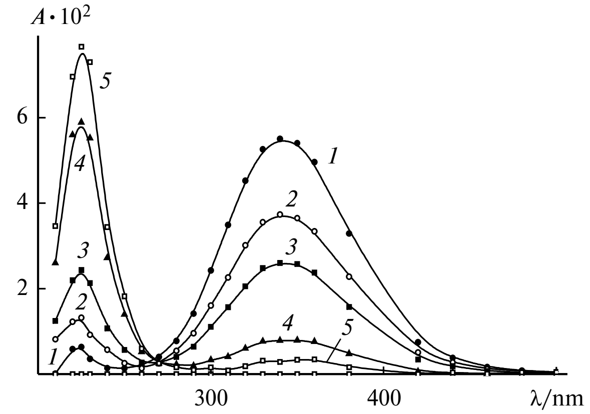

Fig. 4. Absorption spectra of a 1 *M* solution of NaCl (pH 3.3) containing NaI ($5\cdot10^{-6}$ mol L^{-1}) and saturated with N_2O 1 (*1*), 12 (*2*), 50 (*3*), 100 (*4*), and 250 μs (*5*) after electron pulse (pulse duration 40 ns, absorbed dose 16.7 Gy).

termined by the corresponding equilibrium constants (K_{eq}) and reactant concentrations.

Our experiments showed that the pulse irradiation of a 1 *M* solution of NaCl containing NaI ($<1\cdot10^{-5}$ mol L^{-1}) produces the mixed trihalide ion ICl_2^-. This process is illustrated in Fig. 4. The chosen conditions favor ICl_2^- formation to the greatest extent. The low concentration of NaI ($5\cdot10^{-6}$ mol L^{-1}) and a relatively high concentration of the $Cl_2^{\bullet-}$ radical anion formed upon the radiolysis of a 1 *M* solution of NaCl provide the predominant disappearance of the latter due to recombination. It is seen that the disappearance of the absorption at $\lambda = 340$ nm, which belongs to the $Cl_2^{\bullet-}$ radical anion, is accompanied by the appearance of an intense band with a maximum at $\lambda = 225$ nm caused by the trihalide ion ICl_2^- formed in reactions (2)—(4)

$$Cl_2^{\bullet-} + Cl_2^{\bullet-} \longrightarrow Cl_2 + 2\,Cl^-, \qquad (2)$$

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^-, \qquad (3)$$

$$Cl_2 + I^- \longrightarrow ICl_2^-. \qquad (4)$$

All the experimental facts indicate that the reaction of $Cl_2^{\bullet-}$ with I^- affords the $I_2^{\bullet-}$ radical anion.

$$Cl_2^{\bullet-} + I^- \longrightarrow 2\,Cl^- + I^\bullet \qquad (5)$$

$$I^\bullet + I^- \longrightarrow I_2^{\bullet-} \qquad (6)$$

The computer simulation of the process was performed to describe the oxidation of the I^- ion with the $Cl_2^{\bullet-}$ radical anion. The scheme of reactions presented by the equations with the known rate constants, which were used for matching calculations with experimental data, are given in Table 1. The interaction of the $I^\bullet$ atom with the I^- ion producing the $I_2^{\bullet-}$ radical anion and a similar reaction for the $Cl^\bullet$ atom proceed with very high rate constants: $8.8\cdot10^9$ [19,20] and $8.0\cdot10^9$ [14] L mol^{-1} s^{-1}, respectively. The recombination rate constants of the $Cl_2^{\bullet-}$ and $I_2^{\bullet-}$ radical anions were measured for 1 *M* solution of NaCl with pH 3.3 saturated with N_2O. The recombination of the $Cl_2^{\bullet-}$ and $I_2^{\bullet-}$ radical anions affords an equilibrated mixture of the corresponding halogens and trihalide ions. This fact is taken into account in the scheme. Since the calculations were predominantly performed for low concentrations of the I^- ion, the formation of the mixed trihalide ion ICl_2^- *via* reactions (2)—(4), which is important for this case, was taken into account in the scheme. The rate constant of reaction (4) ($3.5\cdot10^9$ L mol^{-1} s^{-1})

Table 1. Reaction rate constants used for the simulation of the kinetics of oxidation of the I^- ion with the radical anion $Cl_2^{\bullet-}$

Reaction	Rate constant	References
$OH^\bullet + Cl^- \to ClOH^{\bullet-}$	$4.3\cdot10^9$ L mol^{-1} s^{-1}	4
$ClOH^{\bullet-} \to OH^\bullet + Cl^-$	$6.1\cdot10^9$ s^{-1}	4
$H^+ + ClOH^{\bullet-} \to Cl^\bullet + H_2O$	$2.1\cdot10^{10}$ L mol^{-1} s^{-1}	4
$Cl^- + Cl^\bullet \to Cl_2^{\bullet-}$	$8.0\cdot10^9$ L mol^{-1} s^{-1}	14
$Cl_2^{\bullet-} \to Cl^\bullet + Cl^-$	$1.1\cdot10^5$ s^{-1}	4
$Cl_2^{\bullet-} + Cl_2^{\bullet-} \to Cl_2 + Cl^-$	$2.6\cdot10^9$ L mol^{-1} s^{-1}	3
$Cl_2 + Cl^- \to Cl_3^-$	$2.0\cdot10^4$ L mol^{-1} s^{-1}	15, 16
$Cl_3^- \to Cl_2 + Cl^-$	$1.1\cdot10^5$ s^{-1}	15, 16
$H^\bullet + Cl_2^{\bullet-} \to Cl^- + HCl$	$7.0\cdot10^9$ L mol^{-1} s^{-1}	17
$H^\bullet + H^\bullet \to H_2$	$7.8\cdot10^9$ L mol^{-1} s^{-1}	18
$Cl_2^{\bullet-} + I^- \to 2\,Cl^- + I^\bullet$	$4.5\cdot10^9$ L mol^{-1} s^{-1}	—*
$I^\bullet + I^- \to I_2^{\bullet-}$	$8.8\cdot10^9$ L mol^{-1} s^{-1}	19, 20
$I_2^{\bullet-} \to I^\bullet + I^-$	$7.0\cdot10^4$ s^{-1}	19, 20
$I^\bullet + I^\bullet \to I_2$	$1.5\cdot10^{10}$ L mol^{-1} s^{-1}	19, 20
$I_2^{\bullet-} + I_2^{\bullet-} \to I_3^- + I^-$	$4.5\cdot10^9$ L mol^{-1} s^{-1}	—*
$I_3^- \to I_2 + I^-$	$7.5\cdot10^6$ s^{-1}	19, 20
$I_2 + I^- \to I_3^-$	$5.6\cdot10^9$ L mol^{-1} s^{-1}	19, 20
$Cl_2 + I^- \to ICl_2^-$	$3.5\cdot10^9$ L mol^{-1} s^{-1}	—*
$ICl_2^- \to ICl^{\bullet-} + Cl^\bullet$	$3.6\cdot10^7$ s^{-1}	13
$ICl^{\bullet-} + Cl^\bullet \to ICl_2^\bullet$	$6.0\cdot10^9$ L mol^{-1} s^{-1}	13

* Data of this work.

was calculated from the kinetics of absorbance appeared at $\lambda = 225$ nm.

The following values were accepted for the initial yields of water radiolysis products[11,21]: $G(e_{aq}^-) = 2.7$, $G(H^+) = 0.6$, and $G(OH^\bullet) = 2.9$. According to known data,[22] the presence of a 1 *M* solution of NaCl or solutions of other halides exerts no significant effect on the initial yields of water radiolysis products. We also took into account that hydrated electrons formed in reaction (1) are transformed into hydroxyl radicals.

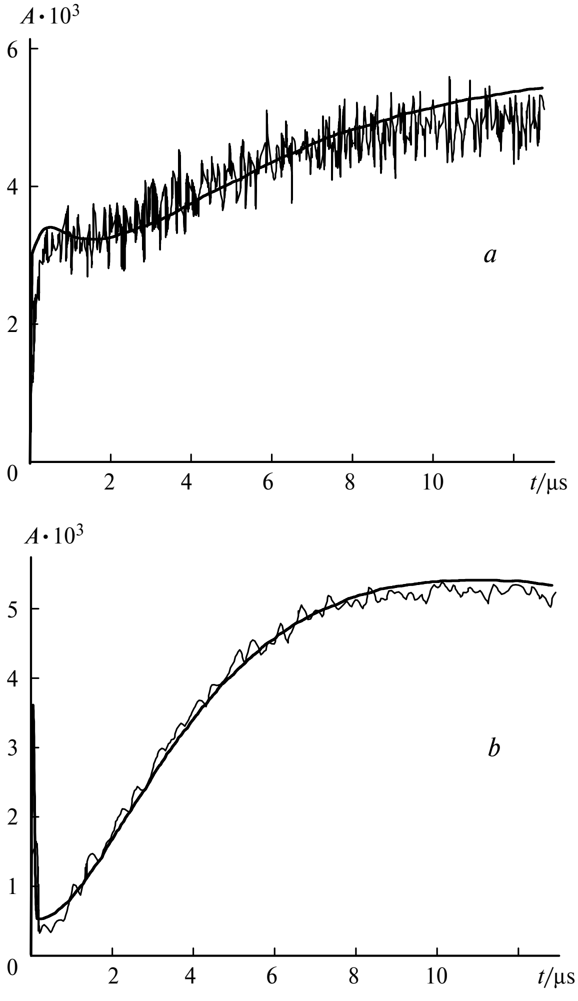

Fig. 5. Comparison of experiment and calculation (smooth line). *a.* Kinetics of the absorbance change at $\lambda = 380$ nm of a 1 *M* solution of NaCl (pH 3.3) containing NaI ($5 \cdot 10^{-5}$ mol L^{-1}) and saturated with N_2O after electron pulse (pulse duration 5 ns, absorbed dose 3.3 Gy). The reaction scheme, rate constant values presented in Table 1, and molar absorption coefficients (ε) equal to 5500, 9400, 3300, and 1000 L mol^{-1} cm^{-1} for $Cl_2^{\bullet-}$, $I_2^{\bullet-}$, I_3^-, and ICl_2^-, respectively, were used for computer simulation. *b.* Kinetics of the absorbance change at $\lambda = 725$ nm of a 1 *M* solution of NaCl (pH 3.3) containing NaI ($5 \cdot 10^{-5}$ mol L^{-1}) and saturated with N_2O after electron pulse (pulse duration 20 ns, absorbed dose 20 Gy). The ε value for $I_2^{\bullet-}$ equal to 2500 L mol^{-1} cm^{-1} was used for computation.

This scheme (see Table 1) well describes the kinetics of changes in the absorption generated by an electron pulse at wavelengths that characterize a change in the concentration of reactants and intermediates decaying and forming during the radiation-chemical process. These are, first of all, the wavelengths corresponding to absorption band maxima of the ion I^- ($\lambda = 225$ nm), radical anions $Cl_2^{\bullet-}$ ($\lambda = 340$ nm) and $I_2^{\bullet-}$ ($\lambda = 380$ and 725 nm), and trihalide ion ICl_2^- ($\lambda = 225$ nm). The known molar absorption coefficients of intermediates involved in the reactions were used for each wavelength.

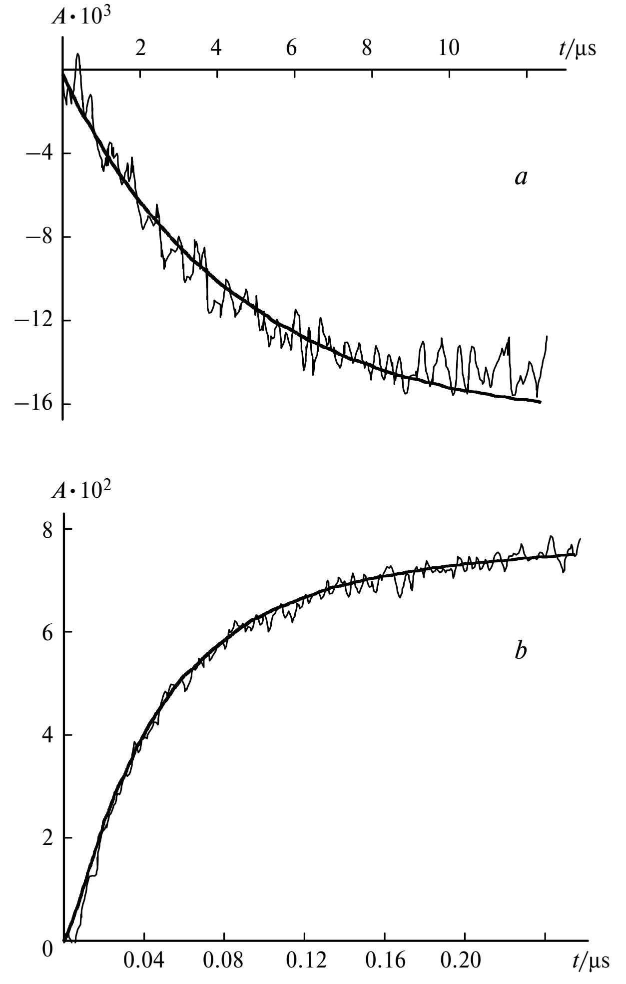

Fig. 6. Comparison of experiment with calculation (smooth line). *a.* Kinetics of the absorbance change at $\lambda = 225$ nm of a 1 *M* solution of NaCl (pH 3.3) containing NaI ($5 \cdot 10^{-5}$ mol L^{-1}) and saturated with N_2O after electron pulse (pulse duration 10 ns, absorbed dose 7.3 Gy). *b.* Kinetics of the absorbance change at $\lambda = 225$ nm of a 1 *M* solution of NaCl (pH 3.3) containing NaI ($2 \cdot 10^{-6}$ mol L^{-1}) and saturated with N_2O after electron pulse (pulse duration 40 ns, absorbed dose 26.7 Gy). In both cases, the reaction scheme, rate constant values given in Table 1, and molar absorption coefficients (ε) equal to 400, 10000, 11000, 250, and 48000 L mol^{-1} cm^{-1} for $Cl_2^{\bullet-}$, Cl_3^-, I^-, $I^\bullet$, and ICl_2^-, respectively, were used for computation.

Figures 5, *a*, *b* and 6, *a* illustrate the agreement between the calculations and experimentally measured change in the absorbance of a 1 *M* solution of NaCl containing NaI ($5.0 \cdot 10^{-4}$ mol L^{-1}) at $\lambda = 380$ (see Fig. 5, *a*), 725 (see Fig. 5, *b*), and 225 nm (see Fig. 6, *a*). The contributions of absorbances from the radical anions $Cl_2^{\bullet -}$, $ClOH^{\bullet -}$, $I^{\bullet}$, and $I_2^{\bullet -}$ involved in chemical transformations are also given in Figs 5 and 6. We can conclude that this scheme agrees satisfactorily with experiment in the time interval of oxidation of the I^- ion with the $Cl_2^{\bullet -}$ radical anion and formation of $I_2^{\bullet -}$ (~12 μs). The calculated rate constant of reaction (5) is $4.5 \cdot 10^9$ L mol^{-1} s^{-1}.

The results of matching of the experimental data for the formation of mixed trihalide ion ICl_2^- in a time interval of ~300 μs are shown in Fig. 6, *a*. Just these times are characteristic of recombination of the $Cl_2^{\bullet -}$ and $I_2^{\bullet -}$ radical anions and formation of the trihalide ions and molecular halogens. The calculated ε value is $4.75 \cdot 10^4$ L mol^{-1} cm^{-1}, which coincides with the earlier measured[13] magnitude.

The results of this work show that the $Cl_2^{\bullet -}$ radical anion in a 1 *M* solution of NaCl oxidize the I^- ion to form the $I^{\bullet}$ atom, which is further transformed into the $I_2^{\bullet -}$ radical anion. However, a mixed radical anion $ClBr^{\bullet -}$ is formed when the Br^- ion is oxidized under the same conditions.[3] In our opinion, this is a consequence of the differences between $E°(Cl_2^{\bullet -}/2\ Cl^-) = 2.09$ V and $E°(Br^{\bullet}/Br^-) = 1.93$ V and $E°(I^{\bullet}/I^-) = 1.33$ V. In the first case, the potential difference is only 0.16 V, which is favorable for the organization of a mixed orbital in $ClBr^{\bullet -}$. In the second case, the difference reaches 0.76 V, and the electron transfer from I^- to $Cl_2^{\bullet -}$ becomes more energetically favorable.

References

1. B. G. Ershov, *Usp. Khim.*, 2004, **73**, 107 [*Russ. Chem. Rev.*, 2004, **73** (Engl. Transl.)].
2. P. Neta, R. E. Huie, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027.
3. B. G. Ershov, M. Kelm, A. V. Gordeev, and E. Janata, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1872.
4. G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1579.
5. D. Zehahi and J. Rabany, *J. Phys. Chem.*, 1972, **76**, 312.
6. P. Wardman, *J. Phys. Chem. Ref. Data*, 1989, **18**, 1711.
7. E. Janata, *Radiat. Phys. Chem.*, 1992, **40**, 437.
8. E. Janata, *Radiat. Phys. Chem.*, 1994, **44**, 449.
9. E. Janata and W. Gutsch, *Radiat. Phys. Chem.*, 1998, **51**, 65.
10. G. L. Hug, *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*, NSRDS—NBS, Washington, 1981.
11. G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.
12. E. Janata and R. H. Schuler, *J. Phys. Chem.*, 1982, **86**, 2078.
13. D. W. Margerum, P. N. Dickson, J. C. Nagy, K. Kumar, C. P. Bowers, and K. D. Fogelman, *Inorg. Chem.*, 1986, **25**, 4900.
14. V. Nagarajan and R. W. Fessenden, *J. Phys. Chem.*, 1985, **89**, 2330.
15. B. G. Ershov, A. V. Gordeev, E. Janata, and M. Kelm, *Mendeleev Commun.*, 2001, **4**, 149.
16. B. G. Ershov, M. Kelm, E. Janata, and A. V. Gordeev, *Radiochem. Acta*, 2002, **90**, 617.
17. S. Navaratnam, B. Parsons, and A. J. Swallow, *Radiat. Phys. Chem.*, 1980, **15**, 159.
18. P. Pagsberg, G. Fenger, and S. O. Nielsen, *J. Phys. Chem.*, 1969, **73**, 1029.
19. H. A. Schwarz and B. H. J. Bielski, *J. Phys. Chem.*, 1986, **90**, 1445.
20. A. J. Elliot, *Can. J. Chem.*, 1992, 7**0**, 1658.
21. I. G. Draganic and Z. D. Draganic, *The Radiation Chemistry of Water*, Academic Press, New York—London, 1971.
22. E. Peled, D. Meisel, and G. Czapski, *J. Phys. Chem.*, 1972, **76**, 3677.

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