Mendeleev Commun., 2002, 12(2), 55–56

Formation and absorption spectra of X_3^- ions upon the radiation-chemical oxidation of Cl^- in the presence of Br^- (Cl, Br = X) in aqueous solution

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10.1070/MC2002v012n02ABEH001561

The formation of Cl_3^-, Cl_2Br^- and $ClBr_2^-$ in the radiation-chemical oxidation of Cl^- ions in an aqueous solution (1–5 M) containing Br^- (10^{-6}–10^{-3} M) ions was studied by pulse radiolysis.

The radiation-chemical oxidation of Cl^- ions in aqueous acid solutions is due to OH radicals, and it results in the formation of Cl_2^- radical anions. The oxidation mechanism was studied in most detail by Jayson *et al.*[1] using a pulse-radiolysis technique. It includes the following reactions:

$$OH + Cl^- \rightleftarrows ClOH^- \qquad (1)$$

$$ClOH^- + H^+ \rightleftarrows Cl + H_2O \qquad (2)$$

$$Cl + Cl^- \rightleftarrows Cl_2^- \qquad (3)$$

It is believed that Cl_2^- disappears in the reaction

$$Cl_2^- + Cl_2^- \longrightarrow Cl_2 + 2Cl^- \qquad (4a)$$

or

$$Cl_2^- + Cl_2^- \longrightarrow Cl_3^- + Cl^- \qquad (4b)$$

The reaction products Cl_2 and Cl_3^- are in the equilibrium

$$Cl_2 + Cl^- \rightleftarrows Cl_3^- \qquad (5)$$

The aim of this work was to detect the formation of the Cl_3^- ion as a result of the radiation-chemical oxidation of Cl^- ions and to study the effect of Br^- ions on this process. For this purpose, we examined weakly acidic ($[H^+] = 5\times10^{-4}$ M) aqueous solutions of NaCl and NaBr saturated with N_2O with the use of pulse radiolysis.

The pulse radiolysis assembly based on a Van de Graaf accelerator with an energy of 3.8 MeV and the computer data processing were described elsewhere.[2–4] Experimental conditions and dosimetry were discussed previously.[5]

Hydrated electrons e_{aq}^- in solutions saturated with N_2O are converted into OH radicals by the following reaction ($k_6 = 9.1\times10^9$ dm^3 mol^{-1} s^{-1}):[6]

$$e_{aq}^- + N_2O + H_2O \longrightarrow OH + N_2 + OH^- \qquad (6)$$

We used concentrated NaCl solutions (≥ 1 M) to shift the equilibrium of reaction (5) to the right and thereby to produce favourable conditions for observing the absorption of Cl_3^-. Figure 1(*a*) demonstrates changes in the absorbance of a 5 M NaCl solution saturated with N_2O (pH 3.3) with time after the action of an electron pulse. After 1 μs, the characteristic absorption band of Cl_2^- with a maximum at 340 nm was observed ($\varepsilon_{Cl_2^-} = 8800$ dm^3 mol^{-1} cm^{-1}).[1] The disappearance of Cl_2^- was accompanied by the appearance of a new band at 220±2 nm, which can be attributed to the formation of the Cl_3^- ion. The absorbance at 220 nm reached a maximum and stable value 0.3 ms after a pulse; this fact indicates that the equilibrium of reaction (5) was rapidly attained. As the concentration of NaCl was decreased from 5 to 1 M, the band intensity at 340 nm on a dose-per-pulse basis remained almost constant. The radiation-chemical yield of Cl_2^- in 1–5 M solutions was 5.3±0.2 ion/100 eV. The optical density (*D*) at 220 nm decreased in the order 0.24; 0.20; 0.17; 0.13 and 0.007 for 5, 4, 3, 2 and 1 M NaCl solutions, respectively, at a dose per pulse of 7.4×10^{16} eV cm^{-3}. That is, the equilibrium of reaction (5) was shifted to the left as the concentration of Cl^- ions was decreased.

The presence of Br^- ions in 1–5 M NaCl solutions even in a very low concentration (≥ 10^{-6} M) considerably affected the absorbance in the UV region. A new band with a maximum at 230±2 nm appeared upon the disappearance of Cl_2^-. Its intensity increased with Br^- concentration and reached a maximum at ~10^{-5} M NaBr. In this case, the rate of appearance of the absorbance increased. Figure 2(*a*) illustrates this process. In the absence of Br^-, the absorbance at 230 nm was very low (< 10%). It is well known[7] that the mixed ion Cl_2Br^- ($\lambda_{max} = 232$ nm) results from the interaction of Cl_2 molecules with Br^- in acidified aqueous solutions. This circumstance allowed us to assign the band observed at 230 nm to the above species. Note that in the case of a 1 M NaCl solution containing 10^{-3} M NaBr a new band with a maximum at 245 nm was formed in the UV region. According to Wang *et al.*,[7] this band was attributed to $ClBr_2^-$.

The absorbance of Cl_2 at 220 nm is negligibly small as compared with the absorbance of Cl_3^-.[7] Therefore, it is believed that

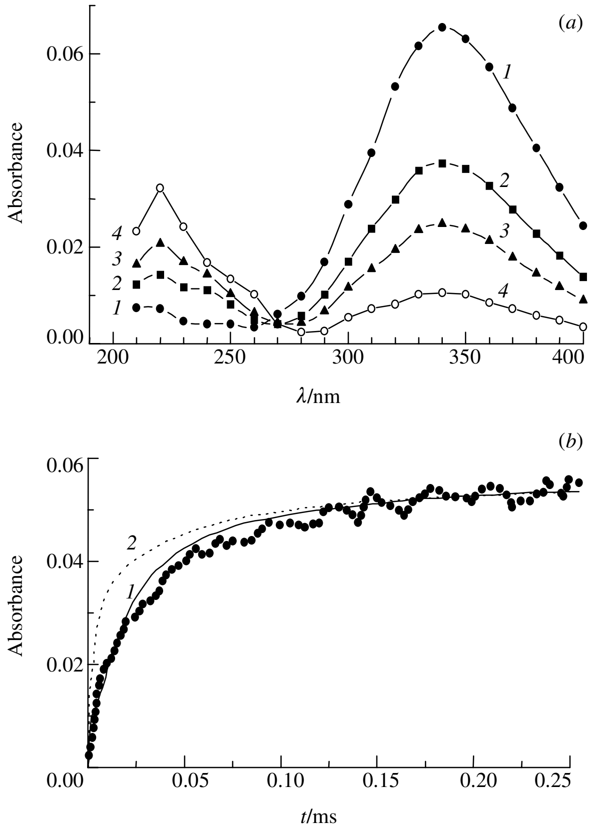

Figure 1 (*a*) Absorption spectra of a 5 M NaCl solution saturated with N_2O (pH 3.3) (*1*) 1, (*2*) 35, (*3*) 80 and (*4*) 250 μs after the action of an electron pulse. Pulse duration, 20 ns. Absorbed dose, 7.4×10^{16} eV cm^{-3}. (*b*) Kinetics of changes in the absorbance at 220 nm in a 5 M NaCl solution saturated with N_2O (pH 3.3) after the action of an electron pulse. Pulse duration, 60 ns. Absorbed dose, 1.7×10^{17} eV cm^{-3}. Points: experimental data. Curves: computer simulation at $k_{5f} = 1.1\times10^5$ s^{-1}, $k_{5b} = 2.0\times10^4$ dm^3 mol^{-1} s^{-1} and $\varepsilon_{220} = 1.35\times10^4$ dm^3 mol^{-1} cm^{-1}. Solid line *1*: Cl_2^- decay by reaction (4a). Dashed line *2*: Cl_2^- decay by reaction (4b) with a rate constant of 1.5×10^9 dm^3 mol^{-1} s^{-1}.

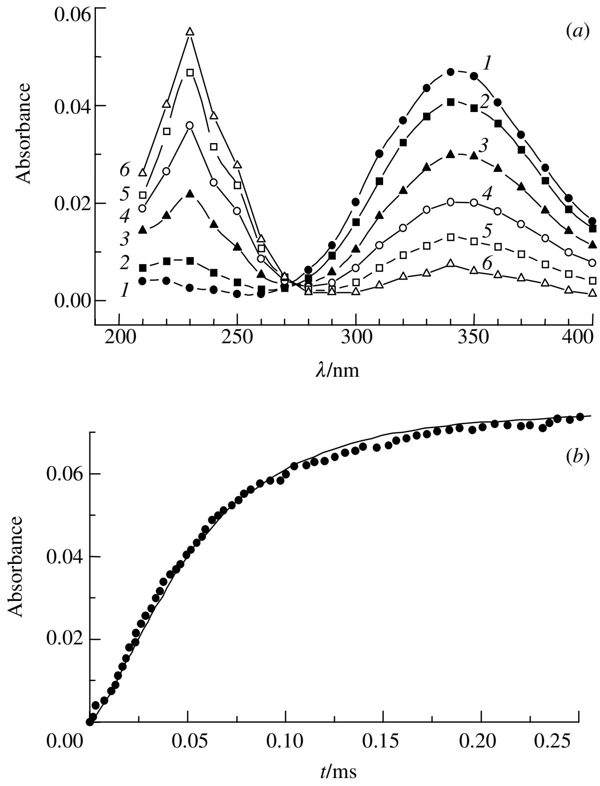

Figure 2 (*a*) Absorption spectra of a 1 M NaCl solution containing 1x10^{-5} M NaBr and saturated with N_2O (pH 3.3) (*1*) 1, (*2*) 8, (*3*) 24, (*4*) 50, (*5*) 100 and (*6*) 250 μs after the action of an electron pulse. Pulse duration, 20 ns. Absorbed dose, 5.4x10^{16} eV cm^{-3}. (*b*) Kinetics of changes in the absorbance at 230 nm in a 1 M NaCl solution containing 1x10^{-5} M NaBr and saturated with N_2O (pH 3.3) after the action of an electron pulse. Pulse duration, 20 ns. Absorbed dose, 7.5x10^{16} eV cm^{-3}. Points: experimental data. Curves: computer simulation at k_{7f} = 6.0x10^9 dm^3 mol^{-1} s^{-1}, k_{7b} = 9.0x10^3 s^{-1}, k_{8f} = = 1.0x10^6 dm^3 mol^{-1} s^{-1}, k_{8b} = 1.7x10^5 s^{-1}; k_9 = 3.0x10^8 dm^3 mol^{-1} s^{-1} and $\varepsilon_{Cl_2Br^-}$ = 3.6x10^4 dm^3 mol^{-1} cm^{-1}.

the value of D_{220} is proportional to the concentration of Cl_3^-. Then, we can write $K_5 = [Cl_3^-]/[Cl_2][Cl^-] = D_x/(D_0 - D_x)[Cl^-]$, where D_x and D_0 are the optical densities of Cl_3^- at 220 nm for a given concentration of Cl^- ions and a Cl^- concentration that approaches infinity, respectively. The use of the experimental dependence of D_{220} on the concentration of Cl^- ions for 1–5 M solutions allowed us to calculate K_5 = 0.18 dm^3 mol^{-1} and ε_{220} = = 1.35x10^4 dm^3 mol^{-1} cm^{-1} (±20%). The value of K_5 is consistent with the constant measured previously in a study of equilibrium (5) in acidic chloride solutions containing chlorine.[7] The value of ε was found to be somewhat higher than 1.04x10^4 dm^3 mol^{-1} cm^{-1}.[7]

The kinetics of disappearance of Cl_2^- and formation of Cl_3^- were fit with the results of computer calculations. In the course of fitting, the values of k_4, k_{5f} and k_{5b} were varied. The decay of Cl_2^- was adequately described by a second-order reaction rate equation, and the value of $\tau_{1/2}$ decreased proportionally to dose per pulse. The value of k_4 for a 5 M NaCl solution was calculated to be equal to 1.5x10^9 dm^3 mol^{-1} s^{-1}. The kinetics of the appearance of the Cl_3^- signal depends on dose per pulse only slightly, and it is inconsistent with the disappearance of Cl_2^-. This fact indicates that the slower step of equilibration by reaction (5) rather than the decay of Cl_2^- is the rate-limiting step in the appearance of the Cl_3^- signal. The kinetic curves of the appearance of absorbance at 220 nm in NaCl solutions can be adequately described [Figure 1(*b*), curve *1*] if we take into account that a Cl_2 molecule is formed upon the disappearance of two Cl_2^-; that is, reaction (4a) takes place and then equilibrium is attained by reaction (5). If reaction (4b) is assumed, the appearance of an optical signal at 220 nm cannot be described at the initial time interval [Figure 1(*b*), curve *2*]. Note that we concluded previously[8] that the Br_3^- ion is formed by an analogous mechanism upon the decay of Br_2^-. It is likely that charges prevent radical anions from approaching and the reaction occurs *via* electron transfer according to scheme (4a). The best fit was attained at k_{5f} = 1.1x10^5 s^{-1} and k_{5b} = 2.0x10^4 dm^3 mol^{-1} s^{-1} [Figure 1(*b*)]; that is, indeed, at $K_5 = k_{5b}/k_{5f}$ equal to 0.18 dm^3 mol^{-1}.

We propose the scheme given below for the formation of Cl_2Br^- in the oxidation of Cl^- in solutions containing Br^- ions. First, it includes the above reactions, which result in the formation of Cl_2 and Cl_3^-. Second, it is supplemented with the reactions that, in accordance with published data,[7] take into account the formation of mixed chlorine and bromine compounds by the interaction of Cl_2 molecules with Br^-.

$$Cl_2 + Br^- \longrightarrow Cl_2Br^- \qquad (7f)$$

$$Cl_2Br^- \longrightarrow Cl_2 + Br^- \qquad (7b)$$

$$Cl_2Br^- \longrightarrow ClBr + Cl^- \qquad (8b)$$

$$ClBr + Cl^- \longrightarrow Cl_2Br^- \qquad (8f)$$

$$Cl_2Br^- + Br^- \longrightarrow ClBr_2^- + Cl^- \qquad (9)$$

The rate constant of the reaction of Cl_2 with Br^- ions in a 1 M HCl solution (k_{7f}) was measured previously with a pulsed-accelerated-flow spectrophotometer (PAF).[7] It was found to be equal to (7.7±1.3)x10^9 dm^3 mol^{-1} s^{-1}. In the optimisation of our experimental data, the best results were obtained with the use of k_{7f} = (6.0±1.0)x10^9 dm^3 mol^{-1} s^{-1} and $K_7 = k_{7f}/k_{7b}$ = (6.7±1.3)x x10^5 dm^3 mol^{-1}. The ratio between the rate constants of forward and backward reactions (8) was taken on a basis of the known $K_8 = k_{8f}/k_{8b}$ equal to (6.0±0.3) dm^3 mol^{-1}.[7] The partial transformation of Cl_2Br^- in the reaction with the Br^- ion to form $ClBr_2^-$ (at 230 nm, ε is 1.8x10^4 dm^3 mol^{-1} cm^{-1}) was also taken into consideration.[7] The rates of $ClBr_2^-$ dissociation into $ClBr + Br^-$ and $Br_2 + Cl^-$ were taken to be low, and they were ignored in the time interval under discussion. The proposed scheme adequately describes the appearance of absorbance at 230 nm in a 1 M NaCl solution in the presence of (1–10)x10^{-6} M Br^- ions at k_{8b} = = 1.7x10^5 s^{-1}, k_{8f} = 1.0x10^6 dm^3 mol^{-1} s^{-1} and k_9 = 3.0x10^8 dm^3 mol^{-1} s^{-1} [Figure 2(*b*)]. The value of ε for Cl_2Br^- was found to be equal to (3.6±0.4)x10^4 dm^3 mol^{-1} cm^{-1}. It is consistent with the published[7] value 3.27x10^4 dm^3 mol^{-1} cm^{-1}. The mechanism of $ClBr_2^-$ formation is much more complicated, and it is beyond the scope of this communication. In addition to Cl_2^-, the radical anions $ClBr^-$ and Br_2^- take part in its formation.[9]

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Received: 20th January 2002; Com. 02/1887