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Kinetics, mechanism and intermediates of some radiation-induced reactions in aqueous solutions

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Contents

I.	Introduction	101
II.	Radiation chemical formation of oxidising and reducing reagents	101
III.	Oxidation of halide ions	102
IV.	Reactions of metal atoms and metal ions in unusual oxidation states	107
V.	Reactions of actinides	108
VI.	Reactions of organic radicals	109
VII.	Conclusion	111

Abstract. The results of pulse radiolysis studies of the kinetics and mechanism of fast one-electron redox reactions of halide ions, metal ions, actinides and other compounds with hydrated electrons, hydroxyl and other radicals and hydrogen atoms and the properties of intermediates formed in these reactions are analysed. The oxidation of a mixture of chloride and bromide ions yields mixed radical anions $ClBr^{-\bullet}$. Data on the formation of metal atoms and ions in unusual and unstable oxidation states by the reduction of metal ions in aqueous solutions and on the reactions involving such ions are presented. It is shown that the reduction of compounds in aqueous solutions with organic radicals takes place through outer- or inner-sphere electron transfer. The bibliography includes 116 references.

I. Introduction

The use of pulse radiolysis has made a considerable contribution to the studies of the kinetics and mechanism of redox reactions and the nature and properties of the short-lived intermediates thus arising. This technique was implemented into the research practice at the Institute of Physical Chemistry of the USSR Academy of Sciences in the early 1970s by initiative and with all-round support from Academician V I Spitsyn and Corresponding member of the Academy A K Pikaev. The description of the method and the results obtained using this method by Russian and foreign researchers before 1980 are considered in detail in a monograph.[1] Data on the properties of metal atoms and metal ions in unusual oxidation states formed upon one-electron reduction or oxidation of metal ions in stable oxidation states in aqueous solutions and on the small clusters formed upon their aggregation are presented in recent reviews.[2–4] The results of pulse radiolysis study of the redox reactions of actinides have been summarised.[5]

This review is a discussion of the results of pulse radiolysis studies of one-electron redox reactions involving diverse inorganic and organic compounds in aqueous solutions obtained mainly during the last 15 years. To cover the problem comprehensively and to provide substantiated interpretation of the data, earlier publications are also considered. Particular attention is paid to the oxidation of halide ions in aqueous solutions. The redox reactions involving chlorine, bromine and iodine are frequently encountered in nature and are used in practice. Thus water disinfection by chlorination still remains the main method for potable water treatment. The production processes involving halogens are widely used in industry. Therefore, considerable attention in the review is paid to the latest advances in the kinetic and mechanistic studies of halogen reactions. Owing to the use of modern investigation techniques for fast redox processes, the formation of mixed short-lived radical anions of the $ClBr^{-\bullet}$ type was detected.[6,7] In addition, characteristic features of a number of one-electron redox reactions of hydrated electrons, hydroxyl radicals, and other inorganic and organic radicals with various compounds in aqueous solutions are analysed.

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II. Radiation chemical formation of oxidising and reducing reagents

When investigating by pulse radiolysis the kinetics and mechanism of one-electron reduction or oxidation of compounds in aqueous solutions and the nature and the properties of the arising intermediates, radical ion species formed upon radiolysis of the solution are taken as the reagents. These species are formed upon ionisation of water molecules on exposure to radiation and in secondary reactions with dissolved compounds. The chemical stage of water radiolysis yields hydrated electrons (e_{aq}^-), hydrogen atoms, protons, and hydroxyl radicals ($OH^\bullet$) as well as hydrogen and hydrogen peroxide molecules. In the general form, the process of water radiolysis can be represented as follows:

$$H_2O \rightsquigarrow e_{aq}^- (2.7) + H^\bullet (0.6) + OH^\bullet (2.9) + \\ + H_2 (0.5) + H_2O_2 (0.7) + H^+ (2.7). \quad (1)$$

The values in parentheses are the initial radiation chemical yields of the products formed in the radiolysis of water and dilute aqueous solutions per 100 eV of absorbed energy for light types of radiation (γ-rays or accelerated electrons for which the linear transfer of energy is insignificant), recorded 10^{-7} s after the action of ionising radiation when the reactions at the sites of local formation of these species ('tracks' and 'spurs') have been completed. The hydrated electrons and hydrogen atoms behave as effective reducing agents. The standard reducing potentials of the

H_2O/e_{aq}^- and $H^+/H^\bullet$ pairs are -2.87 and -2.3 V, respectively.[8] The hydroxyl radical, conversely, is a strong oxidant; its redox potentials in water depend on the pH and amount to 1.9 and 2.73 V for the $OH^\bullet/OH^-$ and $OH^\bullet, H^+/H_2O$ pairs, respectively. These species are used to study one-electron reduction and/or oxidation. However, their simultaneous presence in an aqueous solution initiates the occurrence of both processes and markedly hampers study of the kinetics and the mechanism of redox reactions. Therefore, researchers use such compositions of aqueous solutions which ensure the predominant formation of either oxidising or reducing species. The oxidising radicals $OH^\bullet$ are produced most easily by saturating the solution with nitrous oxide. In a neutral solution, the limiting concentration of the gas under normal conditions equals approximately 0.05 mol litre^{-1}. The exposure to ionising radiation initiates the reaction

$$N_2O + e_{aq}^- + H_2O \longrightarrow N_2 + OH^\bullet + OH^-, \quad (2)$$

whose rate constant equals 9×10^9 litre mol^{-1} s^{-1} (see Ref. 9). As a consequence, hydroxyl radicals are formed in the solution almost alone. It is noteworthy that in the reaction with N_2O, the hydrogen atoms can also be converted into $OH^\bullet$ radicals; however, the rate constant for this reaction is only 1.3×10^4 litre mol^{-1} s^{-1} (see Ref. 9).

Conversely, to create a reducing medium in an aqueous solution, it is necessary to remove the hydroxyl radicals. This is done using solutions containing organic compounds acting as traps for $OH^\bullet$ radicals, *e.g.*, alcohols or salts of organic acids. These compounds also allow binding of hydrogen atoms. For example, upon the addition of isopropyl alcohol or formate ions, the reactions

$$(CH_3)_2CHOH + OH^\bullet\,(H^\bullet) \longrightarrow (CH_3)_2C^\bullet OH + H_2O\,(H_2), \quad (3)$$

$$HCO_2^- + OH^\bullet\,(H^\bullet) \longrightarrow CO_2^{-\bullet} + H_2O\,(H_2), \quad (4)$$

initiated by ionising radiation give rise only to reducing species, namely, hydrated electrons and organic radicals, $(CH_3)_2C^\bullet OH$ or $CO_2^{-\bullet}$. The standard reducing potentials (E°) of some organic radicals used most often are given below.[8]

Species	$CO_2^{-\bullet}$	$(CH_3)_2C^\bullet OH$	$CH_3CH^\bullet OH$	$^\bullet CH_2OH$
E°/V	-1.9	-1.39	-1.25	-1.18

The hydrated electron, the hydroxyl radical, the hydrogen atom, and organic radicals are highly reactive species, and, as a rule, the rates of their interaction with dissolved compounds are controlled by diffusion, the rate constants of the corresponding reactions being about $10^9 - 10^{10}$ litre mol^{-1} s^{-1}. The products of one-electron reduction or oxidation (most often, of a radical nature) are also highly reactive species. Therefore, they are generated and studied in aqueous solutions using a technique of fast processes, first of all, pulse radiolysis with optical or conductometric recording of short-lived products.[1]

III. Oxidation of halide ions

We have already noted that redox reactions involving chlorine, bromine, and iodine are widely used in practice. Therefore, the kinetics and the mechanisms of these reactions are under comprehensive research. Upon photolysis, radiolysis, or other types of physicochemical treatment of aqueous solutions containing halide ions, these ions are oxidised to give first halogen atoms. Subsequently, the process goes through a number of intermediate stages and affords halogen molecules and halogen compounds and the subsequent hydrolysis affords oxygen-containing compounds. The use of pulse radiolysis allows one to study the kinetics and the mechanism of oxidation of halide ions, to establish the nature of the intermediates, in particular, the possibility of formation of mixed radical anions containing atoms of different halogens.

1. Oxidation of Cl^- ions by $OH^\bullet$ radicals

The $OH^\bullet$ radicals are used as the reagent in the kinetic and mechanistic studies of the one-electron oxidation of Cl^- ions in aqueous solutions. In a neutral aqueous solution, Cl^- ions are not oxidised as the reaction is endothermic. Oxidation takes place only in acidic solutions to give $Cl_2^{-\bullet}$ radical anions. The UV spectra of the latter species exhibit an absorption band with a maximum at $\lambda = 340$ nm, the extinction coefficient (ε) at this wavelength being $(8.8 \pm 0.5) \times 10^3$ litre mol^{-1} cm^{-1}. The most detailed pulse radiolysis study of the reaction mechanism has been reported by Jayson *et al.*[10] The process includes the following reversible reactions:

$$Cl^- + OH^\bullet \rightleftharpoons ClOH^{-\bullet}, \quad (5)$$

$$ClOH^{-\bullet} + H^+ \rightleftharpoons Cl^\bullet + H_2O, \quad (6)$$

$$Cl^- + Cl^\bullet \rightleftharpoons Cl_2^{-\bullet}. \quad (7)$$

The $Cl_2^{-\bullet}$ radical anions disappear according to second-order reactions

$$Cl_2^{-\bullet} + Cl_2^{-\bullet} \longrightarrow Cl_2 + 2\,Cl^-, \quad (8)$$

$$OH^\bullet + Cl_2^{-\bullet} \longrightarrow OH^- + Cl_2. \quad (9)$$

It is worth noting that reactions (6) and (8), important in the redox transformations of chlorides, involve charged species, and, hence, they should depend on the ionic strength of the solution. The rate constants for reactions (6), (8) have been measured by pulse radiolysis and their dependences on the ionic strength have been elucidated.[11] In addition, some other reactions involving $Cl_2^{-\bullet}$ radical anions have been studied. This was done using N_2O-saturated weakly acidic (5×10^{-4} M HCl) aqueous solutions of NaCl after a 20-ns pulse of accelerated electrons [the absorbed dose per pulse was $(1.5 \pm 0.3) \times 10^{17}$ eV ml^{-1}]. It was found that after the pulse, optical absorption at $\lambda = 340$ nm passes through a maximum and then diminishes with time. This is due to the formation and subsequent decay of the $Cl_2^{-\bullet}$ radical anions. With an increase in the salt concentration, the rate of disappearance of $Cl_2^{-\bullet}$ increases, which is due to the increase in the ionic strength.

The rate constants for reactions (6), (8), and (9) at different ionic strengths of the solution have been determined by comparing the experimental data with the results of computations performed with the assumption of simultaneous reactions between the products of radiolysis of pure water.[11] The rate constant for reaction (6) increases with an increase in the salt concentration, whereas the rate constant for reaction (8) decreases. This result is consistent with the expected influence of the ionic strength on the rate of reactions between likely and oppositely charged species. Note that high concentrations of dissolved substances in water and the ionic strength of the solution have a pronounced influence on the yields of radiolysis products formed by reaction (1).[12] This must be taken into account when performing calculations. Figure 1 shows the dependences of the rate constants for reactions (6) and (8) on the solution ionic strength both experimental and calculated taking into account the dependence of the reaction rate constant on the activity of the charged species involved in the reaction. The last-mentioned type of dependence can be written as follows (the activity coefficient of the intermediate complex is taken to be unity according to the Brønsted – Bjerrum theory):

$$k = k_0\,\gamma_1^{\nu_1}\gamma_2^{\nu_2} = k_0\gamma_\pm^{\nu}, \quad (10)$$

where k and k_0 are the reaction rate constants for nonzero and zero ionic strengths of the solution, respectively; γ_1 and γ_2 are the activity coefficients of species 1 and 2; $\gamma_\pm$ is the average molal coefficient of activity of the electrolyte; ν_1 and ν_2 are the numbers of particles 1 and 2 involved in the reaction ($\nu = \nu_1 + \nu_2$).

The change in the $\gamma_\pm$ coefficient in the concentration range from 0 to 1 mol litre^{-1} is described adequately by the Debye – Hückel equation:[13]

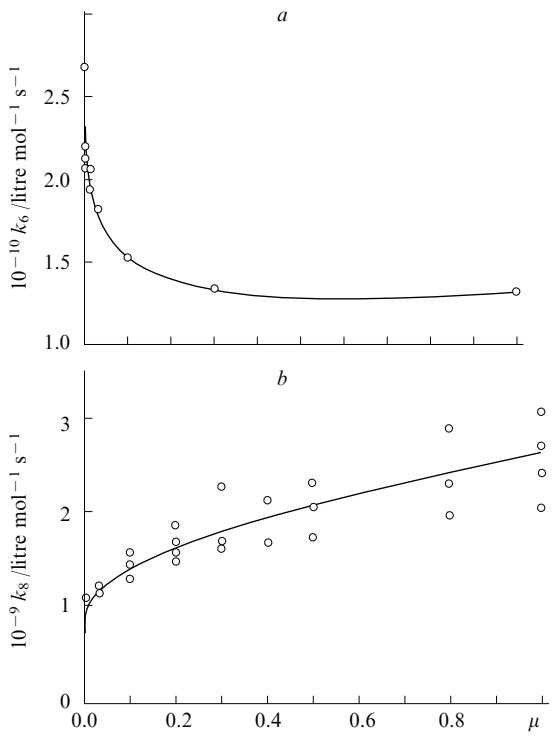


Figure 1. Rate constants for reactions (6) and (8) (k_6 and k_8 , respectively) *vs.* ionic strength of the solution (μ).
The dots correspond to experimental results and the curves, to the calculation from Eqns (10), (11): (*a*) reaction (6); (*b*) reaction (8). The calculation parameters are given in the text.

$$\log \gamma_{\pm} = \frac{A_1 z_1 z_2 \mu^{1/2}}{1 + Ba\mu^{1/2}} + b\mu, \qquad (11)$$

where A and B are coefficients that are constant for the given temperature and solvent; z_1 and z_2 are the charges of the reactants; μ is the ionic strength of the solution for concentrations expressed in mol litre^{-1}; and a and b are experimental parameters.

As can be seen from Fig. 1, the rate constants for reactions (6) and (8) as functions of the solution ionic strength found by optimisation are well described by the Debye–Hückel theory. This fact made it possible to determine their magnitudes for zero ionic strength.[11] For reaction (6), the value $k_6 = 8.3 \times 10^8$ litre mol^{-1} s^{-1} was obtained and the parameters a and b in relation (11) are equal to 0.46 nm and 4.8×10^{-2} litre mol^{-1}, respectively. The value $k_6 = 1.6 \times 10^9$ litre mol^{-1} s^{-1} calculated for an ionic strength of 0.2 is in satisfactory agreement with the rate constant measured in another study,[14] which is equal to 2.0×10^9 litre mol^{-1} s^{-1}. McElroy[15] has studied recombination of the $Cl_2^{-\bullet}$ radical anions produced in the photochemical reaction of $SO_4^{-\bullet}$ with the Cl^- ions. On extrapolation to zero ionic strength, the estimated rate constant for this reaction is 7×10^8 litre mol^{-1} s^{-1}, which is in rather good agreement with the value found in another publication.[11]

For reaction (8) and $\mu = 0$, the value $k_8 = 2.5 \times 10^{10}$ litre mol^{-1} s^{-1} was found; the calculated parameters a and b are 0.42 nm and 0.77 litre mol^{-1}, respectively. The constant $k_8 = 1.4 \times 10^{10}$ litre mol^{-1} s^{-1} calculated for $\mu = 1$ proved to be somewhat lower than the value 2.1×10^{10} litre mol^{-1} s^{-1} reported in another publication.[10]

The rate constant for reaction (9) (k_9) does not depend on the ionic strength of the solution, being equal to 9.2×10^9 litre mol^{-1} s^{-1}. A study of flash photolysis of chloride ions in water[15] gave a value of 1×10^9 litre mol^{-1} s^{-1} for the same rate constant. However, McElroy[15] used conductometry as a technique for recording the variation of the electrical conductivity of the solution, which is not selective in the presence of other reactions involving charged species.

Studies of the kinetics and the mechanism of the oxidation of Cl^- ions with the $OH^\bullet$ radicals made it possible to measure once again the rate constant for a very important reaction between hydrogen atoms and hydrogen peroxide:

$$H^\bullet + H_2O_2 \longrightarrow OH^\bullet + H_2O. \qquad (12)$$

The reported[16] value of 9.0×10^7 litre mol^{-1} s^{-1} did not correspond to the results of computer simulation of the radiation-induced chemical transformations of pure water and water containing added hydrogen and/or hydrogen peroxide and appeared clearly overestimated.[17] Therefore, systematic research into the radiation-induced transformations of argon-saturated chloride solutions (0.1 M HCl) containing hydrogen peroxide has been carried out.[18] Analysis of the kinetics of the additional formation of $Cl_2^{-\bullet}$ radical anions for short radiolysis times (5 μs), caused by the additional generation of the $OH^\bullet$ radicals by reaction (12) allowed Ershov *et al.*[18] to determine the rate constant for this reaction $k_{12} = 3.5 \times 10^7$ litre mol^{-1} s^{-1}. This value is consistent with the constant found for the decay of hydrogen atoms by EPR.[19] For long radiolysis times (250 μs), recombination of the $Cl_2^{-\bullet}$ radical anions and their reaction with H_2O_2 are the predominant processes

$$H_2O_2 + Cl_2^{-\bullet} \longrightarrow 2\,HCl + O_2^{-\bullet}. \qquad (13)$$

The role of reaction (13) increases with an increase in the concentration of hydrogen peroxide. When the H_2O_2 content is $\geqslant 5 \times 10^{-2}$ mol litre^{-1}, the kinetics of the decay of $Cl_2^{-\bullet}$ absorption is better described by a pseudo-first-order equation, which indicates that these radical anions mainly disappear by reaction (13). Modelling of the kinetic curves for the decay of the $Cl_2^{-\bullet}$ species allowed Ershov *et al.*[11] to determine the rate constant for reaction (13): $k_{13} = 9.5 \times 10^5$ litre mol^{-1} s^{-1}. For solutions containing hydrogen peroxide, it was necessary to include additional steps taking into account the reactions of $H^\bullet$ and $OH^\bullet$ with H_2O_2 and with the $HO_2^\bullet$ radical.

The results of a kinetic study of the redox reactions of Cl^- ions in aqueous solutions induced by ionising radiolysis are summarised in Table 1.

Table 1. Rate constants (k) for the oxidation of the Cl^- and Br^- ions.

Reaction	k /litre mol^{-1} s^{-1}	Ref.
$OH^\bullet + Cl^- \longrightarrow ClOH^{-\bullet}$	4.3×10^9	10
$ClOH^{-\bullet} \longrightarrow OH^\bullet + Cl^-$	6.1×10^9 (see [a])	10
$H^+ + ClOH^{-\bullet} \longrightarrow Cl^\bullet + H_2O$	2.5×10^{10}	10
$Cl^- + Cl^\bullet \longrightarrow Cl_2^{-\bullet}$	8.0×10^9	20
$Cl_2^{-\bullet} \longrightarrow Cl^\bullet + Cl^-$	1.1×10^5 (see [a])	10
$Cl_2^{-\bullet} + Cl_2^{-\bullet} \longrightarrow Cl_3^- + Cl^-$	8.3×10^8	11
$H^\bullet + Cl_2^{-\bullet} \longrightarrow Cl^- + HCl$	7.0×10^9	14
$OH^\bullet + Cl_2^{-\bullet} \longrightarrow OH^- + Cl_2$	9.2×10^9	11
$H_2O_2 + Cl_2^{-\bullet} \longrightarrow 2\,HCl + O_2^{-\bullet}$	9.5×10^5	11
$Cl_2^{-\bullet} + Br^- \longrightarrow ClBr^{-\bullet} + Cl^-$	4.0×10^9	7
$ClBr^{-\bullet} + Cl^- \longrightarrow Cl_2^{-\bullet} + Br^-$	1.1×10^2	7
$ClBr^{-\bullet} \longrightarrow Cl^- + Br^\bullet$	8.5×10^7 (see [a])	7
$Cl^- + Br^\bullet \longrightarrow ClBr^{-\bullet}$	1.0×10^{10}	7
$ClBr^{-\bullet} + Br^- \longrightarrow Br_2^{-\bullet} + Cl^-$	8.0×10^9	7
$Br_2^{-\bullet} + Cl^- \longrightarrow ClBr^{-\bullet} + Br^-$	4.3×10^6	7
$Br_2^{-\bullet} \longrightarrow Br^\bullet + Br^-$	4.6×10^4 (see [a])	21, 22
$Br^\bullet + Br^- \longrightarrow Br_2^{-\bullet}$	1.0×10^{10}	21, 22
$Br_2^{-\bullet} + Br_2^{-\bullet} \longrightarrow Br_3^- + Br^-$	3.4×10^9	7

[a] The rate constant is expressed in s^{-1}.

2. Oxidation of Br^- ions by $Cl_2^{-\bullet}$ radical anions and the formation of $ClBr^{-\bullet}$ radical anions

Most often, chlorine is accompanied by bromine and/or iodine impurities. Therefore, the redox reactions with chlorine are accompanied by chemical transformations of these halogens. Indeed, chlorination of water yields bromate ion BrO_3^- (see Ref. 21), which is carcinogenic. Lots of other examples can also be cited. This underlines the topicality of comprehensive investigation of the influence of bromine and iodine impurities on the oxidation of chlorine.

Radiation-induced or photochemical oxidation of Br^- ions in aqueous solutions is known [22] to give $Br_2^{-\bullet}$ radical anions [$\lambda_{max} = 360$ nm, $\varepsilon = (9.9\pm0.6)\times10^3$ litre mol^{-1} cm^{-1}]. However, their spectra, unlike the spectra of the $Cl_2^{-\bullet}$ radical anions, exhibit also a weak optical absorption in the region of 650–700 nm. The standard reduction potentials of the $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ radical anions are as follows: $E^\circ(Cl_2^{-\bullet}/2\,Cl^-) = 2.30$ V; $E^\circ(Br_2^{-\bullet}/2\,Br^-) = 1.66$ V;[8] hence, these species behave as rather strong oxidants. The rate constants for many reactions of one-electron oxidation of organic and inorganic compounds involving these radical anions have been measured by pulse radiolysis and photolysis.[23] Comparison of the $E^\circ(Cl_2^{-\bullet}/2\,Cl^-)$ value with $E^\circ(Br_2^{-\bullet}/2\,Br^-)$ and also with $E^\circ(Br^\bullet/Br^-) = 2.0$ V may indicate that the $Cl_2^{-\bullet}$ radical anions are able to oxidise Br^- ions in an aqueous solution to give $Br_2^{-\bullet}$ radical anions.

Recently, oxidation of the Br^- ions by $Cl_2^{-\bullet}$ radical anions [6, 7, 24] has been studied by pulse radiolysis. The interest in this important reaction was stimulated not only by fundamental but also by practical problems. First of all, this was due to the need to study the oxidation of bromine during water chlorination and the radiation-induced chemical reactions in natural water near sites of nuclear waste disposal, first of all, in salt mines (see for example, Refs 25–27). Apart from substantial amounts of chlorides, this water contains bromides. Chemical transformations of the latter initiated by ionising radiation can substantially influence the ultimate composition of the obtained products and, hence, the safety of waste storage. The studies showed that in N_2O-saturated concentrated solutions of chlorides (1 M NaCl, pH 3.3) containing 1.0×10^{-3} mol litre^{-1} of bromine, oxidation of Br^- ions by $Cl_2^{-\bullet}$ radical anions proceeds at a high rate and ends in the formation of the $Br_2^{-\bullet}$ radical anions.[6, 7] At $[Br^-] \leqslant 1.0\times10^{-4}$ mol litre^{-1}, mixed radical anions $ClBr^{-\bullet}$ are produced. Similar mixed intermediates ($ClSCN^{-\bullet}$ and $BrSCN^{-\bullet}$ radical anions) have been detected previously by pulse radiolysis upon oxidation of chloride [28] and bromide ions,[29] respectively, in the presence of small amounts of the SCN^- ions added. The $ClBr^{-\bullet}$ radical anions arise and coexist in an equilibrium with the $Cl_2^{-\bullet}$ and $Br_2^{-\bullet}$ species, in accordance with the reactions

$$Cl_2^{-\bullet} + Br^- \rightleftharpoons ClBr^{-\bullet} + Cl^-, \quad (14)$$

$$ClBr^{-\bullet} + Br^- \rightleftharpoons Br_2^{-\bullet} + Cl^-. \quad (15)$$

Redox reactions (14) and (15) can be written in the following way:
reaction (14),

$$Cl_2^{-\bullet} + e^- \longrightarrow Cl^- + Cl^-,$$

$$Cl^- + Br^- \longrightarrow ClBr^{-\bullet} + e^-;$$

reaction (15),

$$ClBr^{-\bullet} + e^- \longrightarrow Br^- + Cl^-,$$

$$Br^- + Br^- \longrightarrow Br_2^{-\bullet} + e^-.$$

The corresponding redox potentials are $\Delta E_{14}^\circ = E^\circ(Cl_2^{-\bullet}/2\,Cl^-) - E^\circ(ClBr^{-\bullet}/Cl^-,Br^-)$ and $\Delta E_{15}^\circ = E^\circ(ClBr^{-\bullet}/Cl^-,Br^-) - E^\circ(Br_2^{-\bullet}/2\,Br^-)$. The ΔE° value can be expressed *via* the equilibrium constant (K) as $\Delta E^\circ = 0.059 \log K$. By using the known values, $E^\circ(Br_2^{-\bullet}/2\,Br^-) = 1.66$ V and $E^\circ(Cl_2^{-\bullet}/2\,Cl^-) = 2.3$ V, one can find [2, 4] $K_{14}\times K_{15} = 7.0\times10^{10}$.

Optimisation of the time dependence observed in the optical spectra for the intensity of the signal at 700 nm, which is composed of the absorption of the $ClBr^{-\bullet}$ and $Br_2^{-\bullet}$ radical anions, has given [7] the following values: $K_{14} = 3.78\times10^7$, $K_{15} = 1.85\times10^3$, $\varepsilon_{ClBr^{-\bullet}} = 110$ litre mol^{-1} cm^{-1} (for $\lambda =$ 700 nm). The K_{14} and K_{15} values were used to calculate the oxidation potential for the $ClBr^{-\bullet}/Cl^-,Br^-$ pair, which proved to be 1.85 V. As was to be expected, this value is intermediate between the potentials of $Br_2^{-\bullet}$ (1.66 V) and $Cl_2^{-\bullet}$ (2.30 V).

For the equilibria,

$$ClBr^{-\bullet} \rightleftharpoons Br^\bullet + Cl^- \quad (16)$$

and

$$Br_2^{-\bullet} \rightleftharpoons Br^\bullet + Br^-, \quad (17)$$

the relation $K_{15} = K_{16}/K_{17}$ is valid. Using the known [30, 31] $K_{17} = 4.6\times10^{-6}$ mol litre^{-1} and the equilibrium constant $K_{15} = 1.85\times10^3$ determined by Ershov *et al.*,[7] we get $K_{16} = 8.5\times10^{-3}$ mol litre^{-1}. Similarly, for the equilibria,

$$ClBr^{-\bullet} \rightleftharpoons Cl^\bullet + Br^- \quad (18)$$

and

$$Cl_2^{-\bullet} \rightleftharpoons Cl^\bullet + Cl^-, \quad (19)$$

it can be written that $K_{14} = K_{19}/K_{18}$. Using the above-indicated value $K_{14} = 3.78\times10^7$ and the reported [20] constant $K_{19} = 5.3\times10^{-6}$ mol litre^{-1}, one can calculate the value $K_{18} = 1.4\times10^{-13}$ mol litre^{-1}. Comparison of the values of K_{16} and K_{18} shows that the probability of the decay of the $ClBr^{-\bullet}$ species according to reaction (18) is low compared to that by reaction (16).

Computer simulation of the experimental data on the oxidation kinetics of the Br^- ions by the $Cl_2^{-\bullet}$ radical anions has been reported.[7] The calculated rate constants for the formation of the $Cl_2^{-\bullet}$ radical anions and for their reaction with Br^- ions and the known rate constants of other reactions are presented in Table 1. It was found [7] that the set of reactions proposed describes

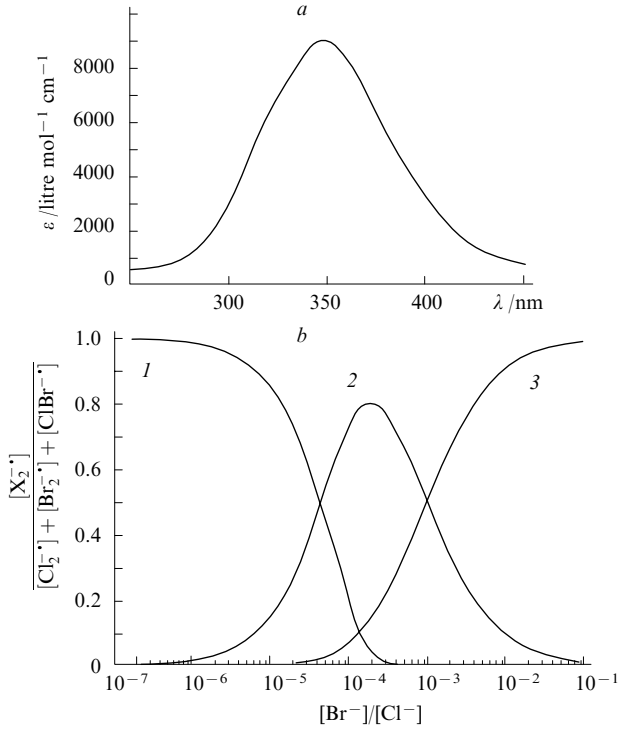


Figure 2. (*a*) Absorption spectrum of the $ClBr^{-\bullet}$ radical anion. (*b*) Equilibrium concentrations of the $X_2^{-\bullet} = Cl_2^{-\bullet}$ (*1*), $ClBr^{-\bullet}$ (*2*) and $Br_2^{-\bullet}$ (*3*) radical anions in solution *vs.* $[Br^-]/[Cl^-]$ [7, 24] ratio.

adequately the kinetics of variation of the optical absorption generated by an electron pulse at all wavelengths. For each wavelength, known [9,22] extinction coefficients were used for the $Cl_2^{-\bullet}$, $ClOH^{-\bullet}$ and $Br_2^{-\bullet}$ radical anions, while the $\varepsilon_{ClBr^{-\bullet}}$ values were calculated.

Figure 2*a* shows the absorption spectrum of the $ClBr^{-\bullet}$ radical anions obtained by matching the experimental data to the calculations in terms of the set of chemical reactions indicated in Table 1.[7] The spectrum is a broad absorption band with a maximum at $\lambda = 350\pm3$ nm and with the coefficient ε at this wavelength equal to 9300 ± 200 litre mol^{-1} cm^{-1}. Thus, the optical characteristics of $ClBr^{-\bullet}$ prove to be intermediate between the corresponding characteristics of the $Cl_2^{-\bullet}$ ($\lambda_{max} = 340$ nm and $\varepsilon = 8800$ litre mol^{-1} cm^{-1}) [10] and $Br_2^{-\bullet}$ radical anions ($\lambda_{max} = 360$ nm and $\varepsilon = 9900$ litre mol^{-1} cm^{-1}).[32]

Figure 2*b* presents an illustration of the dependence of the ratio of the equilibrium concentrations of the $Cl_2^{-\bullet}$, $ClBr^{-\bullet}$, and $Br_2^{-\bullet}$ radical anions on the concentration ratio of the Cl^- and Br^- ions.[7,24] The $Cl_2^{-\bullet}$ radical anions oxidise the Br^- ions to give $ClBr^{-\bullet}$ and $Br_2^{-\bullet}$ radical anions. As the concentration of Br^- increases, the equilibrium shifts towards $Br_2^{-\bullet}$.

3. Decay of the $Cl_2^{-\bullet}$ radical anions and the formation of molecular chlorine and the Cl_3^- anions

The oxidation of chloride ions in water gives rise to molecular chlorine as a result of recombination of the $Cl_2^{-\bullet}$ radical anions arising at an intermediate stage

$$Cl_2^{-\bullet} + Cl_2^{-\bullet} \longrightarrow Cl_3^- + Cl^- \qquad (20a)$$

or

$$Cl_2^{-\bullet} + Cl_2^{-\bullet} \longrightarrow Cl_2 + 2\,Cl^-. \qquad (20b)$$

The Cl_3^- ion exists in equilibrium with molecular chlorine

$$Cl_3^- \rightleftharpoons Cl_2 + Cl^-. \qquad (21)$$

Zimmerman and Strong [33] have measured the absorption spectra of Cl_3^- and Cl_2 in neutral and acidic aqueous solutions containing dissolved chlorine. The spectrum of Cl_3^- ions is a broad optical band with a maximum at $\lambda \approx 220$ nm and $\varepsilon = 1\times10^4$ litre mol^{-1} cm^{-1}. These data were confirmed by more advanced investigation techniques.[34] It was found that for Cl_3^-, the extinction coefficient at $\lambda = 220$ nm equals 1.04×10^4 litre mol^{-1} cm^{-1}; the spectrum also exhibits a weak peak at 320 nm ($\varepsilon = 180$ litre mol^{-1} cm^{-1}). The value of ε at 330 nm for chlorine does not exceed 70 litre mol^{-1} cm^{-1}. The stability constant of the Cl_3^- ions (K_{21}) was found to be 0.18 ± 0.02 mol litre^{-1} (see Ref. 34). Hence, the equilibrium of reaction (21) shifts towards the trichloride ions Cl_3^- only when the content of the Cl^- ions in solution is very high.

Until recently, trichloride ions have not been detected as products of photochemical or radiation chemical oxidation of Cl^- ions or transformations of $Cl_2^{-\bullet}$ radical anions in aqueous solutions. It was not clear which species, Cl_3^- or Cl_2, arises as the primary product of the transformations of the $Cl_2^{-\bullet}$ radical anions by reactions (20a) and (20b), respectively. This and some other questions were answered by Ershov *et al.*,[24] who suggested, proceeding from the value $K_{21} = 0.18\pm0.02$ mol litre^{-1}, that Cl_3^- can be found in relatively concentrated ($\geqslant 1$ M) solutions of Cl^-. This conclusion was confirmed experimentally.[24] A weak absorption with a maximum at 220 nm was found to appear in the spectrum of a 1 M solution of NaCl during the decay of the $Cl_2^{-\bullet}$ radical anions, the signal intensity being higher for higher concentrations of the salt. A rather clear-cut optical absorption was detected in the spectra of a 5 M solution of NaCl. It seemed reasonable to relate the appearance of the signal at 220 nm to the formation of Cl_3^- ions upon the decay of $Cl_2^{-\bullet}$. The rate of disappearance of the signal increased with an increase in the absorbed dose per pulse. The kinetics of the decay of the $Cl_2^{-\bullet}$ radical anions was well described by a second-order equation and the $\tau_{1/2}$ value decreased in proportion with the dose per pulse. Unlike the decay of the $Cl_2^{-\bullet}$ species, the appearance of Cl_3^- ions depended only little on the dose per pulse and could not be described by simple first- or second-order kinetics. The $\tau_{1/2}$ values did not change much upon variation of the absorbed dose per pulse. All this indicated that the formation of the signal from Cl_3^- ions is not limited by the decay of the $Cl_2^{-\bullet}$ radical anions but is limited by another process, which is slower. It was found [24] that the slow process of establishing the equilibrium in reaction (21) is the rate-limiting step in the formation of Cl_3^- ions. Analysis of the kinetics of appearance of the Cl_3^- ions allowed the researchers to determine the rate constants for the forward (the subscript f) and back (the subscript b) reactions (21) to be $k_{21f} = 1.1\times10^5$ s^{-1}, $k_{21b} = 2.0\times10^4$ litre mol^{-1} s^{-1}. The equilibrium constant of reaction (21) obtained by this optimisation, $K_{21} = k_{21b}/k_{21f}$, amounts to 0.18 litre mol^{-1}, which is in full agreement with the value measured previously.[33,34] Thus, the reaction between two $Cl_2^{-\bullet}$ species is most likely to afford the Cl_2 molecule. Apparently, the like charges of the radical anions prevent these species from approaching each other and the reaction occurs at a certain distance between them upon an electron transfer by reaction (20b). The subsequent appearance of the Cl_3^- ion is due to establishment of equilibrium (21).

4. Oxidation of the Br^- ions and formation of the Br_3^- anions

The radiation-induced oxidation of Br^- ions by $OH^\bullet$ radicals in acidic aqueous solutions gives rise to $Br_2^{-\bullet}$ radical anions.[22,32] The oxidation mechanism is similar to the mechanism considered above for chlorides. The pattern of transformations of bromide ions includes the following reactions:

$$Br^- + OH^\bullet \rightleftharpoons BrOH^{-\bullet}, \qquad (22)$$

$$BrOH^{-\bullet} + H^+ \rightleftharpoons Br^\bullet + H_2O, \qquad (23)$$

$$Br^- + Br^\bullet \rightleftharpoons Br_2^{-\bullet}, \qquad (24)$$

$$Br^\bullet + OH^- \rightleftharpoons BrOH^{-\bullet}, \qquad (25)$$

$$BrOH^{-\bullet} + Br^- \longrightarrow Br_2^{-\bullet} + OH^-. \qquad (26)$$

The mechanism of recombination of $Br_2^{-\bullet}$ radical anions has been studied.[31] It was found that disappearance of $Br_2^{-\bullet}$ absorption, which was observed 1 μs after the action of an electron pulse on a 0.1 M solution of NaBr (N_2O, pH 3.3), is accompanied by the formation of a new band with a maximum at 265 nm. This is due to the formation of Br_3^- ions in accordance with the reactions:

$$Br_2^{-\bullet} + Br_2^{-\bullet} \longrightarrow Br_2 + 2\,Br^-, \qquad (27)$$

$$Br_2 + Br^- \rightleftharpoons Br_3^-. \qquad (28)$$

For bringing the experimental data in correspondence with the results of computation, the following rate constants for reactions (22)–(26) were used:[22,35] (the subscripts f and b refer to the forward and back reaction, respectively): $k_{22f} = 1.06\times10^{10}$ litre mol^{-1} s^{-1}; $k_{22b} = 3.3\times10^7$ s^{-1}; $k_{23f} = 4.4\times10^{10}$ litre mol^{-1} s^{-1}; $k_{23b} = 1.4$ s^{-1}; $k_{24f} = 1.0\times10^{10}$ litre mol^{-1} s^{-1}; $k_{24b} = 4.6\times10^4$ s^{-1}; $k_{25f} = 1.3\times10^{10}$ litre mol^{-1} s^{-1}; $k_{25b} = 4.2\times10^6$ s^{-1}; $k_{26} = 1.9\times10^8$ litre mol^{-1} s^{-1}. The values of k_{27}, k_{28f} and k_{28b} were varied during optimisation. It was found [32] that the formation and disappearance of the $Br_2^{-\bullet}$ radical anions is described adequately using the values $\varepsilon_{Br_2^{-\bullet}} = 9900$ litre mol^{-1} cm^{-1} (see Ref. 22) and $k_{27} = 3.0\times10^9$ litre mol^{-1} s^{-1}. The resulting k_{27} value is in good agreement with the experimental rate constant measured for dilute solutions of Br^- ions, which is equal to 2.2×10^9 litre mol^{-1} s^{-1} (see Ref. 23). The agreement for the kinetics of appearance of the Br_3^- anions is attained for $k_{28f} = 9.6\times10^8$ litre mol^{-1} s^{-1}, $k_{28b} = 5.5\times10^7$ s^{-1} and $\varepsilon_{Br_3^-} = 4.4\times10^4$ litre mol^{-1} cm^{-1}. The equilibrium constant for reaction (28) calculated using the k_{28f} and k_{28b} as $K_{28} = k_{28f}/k_{28b}$ amounts to 17.4 litre mol^{-1}. Thus, the obtained values of $\varepsilon_{Br_3^-}$ and K_{28} are in good agreement with the extinction coefficient and the equilibrium constant determined [34] in a study of reaction (28)

in slightly acidic solutions of molecular bromine and Br^- ions, which are equal to 4.1×10^4 litre mol^{-1} cm^{-1} and 16.1 litre mol^{-1}, respectively.

5. Chlorine and bromine mixed trihalide ions

It was established [24, 36] that the presence of even very small amounts ($\geqslant 10^{-6}$ mol litre^{-1}) of Br^- ions in concentrated (1–5 M) solutions of NaCl results in substantial changes in the oxidation mechanism of chloride ions. During the decay of $Cl_2^{-\bullet}$ radical anions, Cl_3^- ions are no longer formed but, instead, the reaction gives a new intermediate characterised by an intense absorption band. As the bromine concentration increases (up to 10^{-3} mol litre^{-1} NaBr), new products responsible for intense optical bands with maxima at 230 and 245 nm are formed successively. On a further increase in the bromine content in the solution, an absorption band with a maximum at 265 nm corresponding to the Br_3^- ion appears in parallel with the disappearance of the $Cl_2^{-\bullet}$, $ClBr^{-\bullet}$ and $Br_2^{-\bullet}$ radical anions.

Analysis of the variation of the spectral pattern in the UV region demonstrates the complexity of the chemical transformations involved, in particular, transition from Cl_3^- ($\lambda_{max} = 220$ nm) to Br_3^- ($\lambda_{max} = 265$ nm) through consecutive formation of mixed chlorine/bromine oxidation products. It was shown [24, 36] that the absorption bands with maxima at 230 and 245 nm refer to mixed trihalide ions, Cl_2Br^- and $ClBr_2^-$, respectively. It has been noted previously [34] that these species are also formed in the reactions of Cl_2 and ClBr molecules with Cl^- and Br^- ions in acidified aqueous solutions.

A reaction scheme for the formation of Cl_2Br^- ions upon radiation-induced chemical oxidation of chloride ions in slightly acidic aqueous solutions has been proposed.[24] First, it includes reactions (20a) and (21) we considered above (with the rate constants found for them), which give rise to molecular chlorine and Cl_3^-. Second, it is supplemented [34] by steps yielding mixed compounds of chlorine and bromine upon reactions of Cl_2 molecules with Br^- ions:

$$Cl_2 + Br^- \longrightarrow Cl_2Br^-,\ k_{29f} = 6.0 \times 10^9 \text{ litre mol}^{-1}\text{ s}^{-1}; \quad (29f)$$

$$Cl_2Br^- \longrightarrow Cl_2 + Br^-,\ k_{29b} = 9.0 \times 10^3\ \text{s}^{-1}; \quad (29b)$$

$$ClBr + Cl^- \longrightarrow Cl_2Br^-,\ k_{30f} = 1.0 \times 10^6 \text{ litre mol}^{-1}\text{ s}^{-1}; \quad (30f)$$

$$Cl_2Br^- \longrightarrow ClBr + Cl^-,\ k_{30b} = 1.7 \times 10^5\ \text{s}^{-1}; \quad (30b)$$

$$Cl_2Br^- + Br^- \longrightarrow ClBr_2^- + Cl^-,\ k_{31} = 3.0 \times 10^8 \text{ litre mol}^{-1}\text{ s}^{-1}. \quad (31)$$

Previously, the rate constant for the reaction of Cl_2 with Br^- ions in 1 M HCl (k_{29f}) was measured to be $(7.7 \pm 1.3) \times 10^9$ litre mol^{-1} s^{-1}. The order of magnitude of the constant shows that this reaction is controlled by diffusion. By modelling in terms of this set of reactions, the constants $k_{29b} = (6.0 \pm 1.0) \times 10^9$ litre mol^{-1} s^{-1} and $K_{29} = k_{29f}/k_{29b} = (6.7 \pm 1.3) \times 10^5$ litre mol^{-1} were determined.[24] The ratio of the constants for the forward and back reactions (30) was selected proceeding from the known $K_{30} = k_{30f}/k_{30b}$ value, equal to (6.0±0.3) litre mol^{-1} (see Ref. 34). The partial transformation of Cl_2Br^- into $ClBr_2^-$ upon the reaction with Br^- ions has also been taken into account (the extinction coefficient of the last-mentioned trihalide at $\lambda = 230$ nm is 1.8×10^4 litre mol^{-1} cm^{-1}). The proposed set of reactions [24] describes adequately the radiation-induced oxidation of chloride ions in aqueous solutions containing some bromide ions. The extinction coefficients of the Cl_2Br^- (230 nm) and Br_2Cl^- (245 nm) trihalide ions were calculated to be $\varepsilon = (3.6 \pm 0.4) \times 10^4$ and $(2.2 \pm 0.3) \times 10^4$ litre mol^{-1} cm^{-1}, respectively. These values are in good agreement with the values 3.27×10^4 and 2.49×10^4 litre mol^{-1} cm^{-1} measured in another study,[34] where the trihalides Cl_2Br^- and Br_2Cl^- were prepared by reactions of Cl_2 and ClBr with Br^- ions.

Table 2. Rate constants (k) and equilibrium constants (K) for the formation of trihalide ions X_3^- (X = Cl, Br) and optical characteristics of the X_3^- ions [24, 36]

Reaction	k (see [a])	K (see [b])	X_3^-	λ_{max} /nm	ε (see [c])
$Cl_2 + Cl^- \longrightarrow Cl_3^-$	2.0×10^4	0.18	Cl_3^-	220	1.3×10^4
$Cl_3^- \longrightarrow Cl_2 + Cl^-$	1.1×10^5 (see [d])				
$Cl_2 + Br^- \longrightarrow Cl_2Br^-$	6.0×10^9	6.7×10^5	Cl_2Br^-	230	3.6×10^4
$Cl_2Br^- \longrightarrow Cl_2 + Br^-$	9.0×10^3 (see [d])				
$ClBr + Cl^- \longrightarrow Cl_2Br^-$	1.0×10^6	6.0			
$Cl_2Br^- \longrightarrow ClBr + Cl^-$	1.7×10^5 (see [d])				
$Cl_2Br^- + Br^- \longrightarrow ClBr_2^- + Cl^-$	3.0×10^8		$ClBr_2^-$	245	2.2×10^4
$Br_2 + Br^- \longrightarrow Br_3^-$	9.6×10^8	17.5	Br_3^-	265	4.4×10^4
$Br_3^- \longrightarrow Br_2 + Br^-$	5.5×10^7 (see [d])				

[a] The rate constant is expressed in litre mol^{-1} s^{-1}; [b] the equilibrium constant is expressed in litre mol^{-1}; [c] the extinction coefficient is expressed in litre mol^{-1} cm^{-1}; [d] the constant is in s^{-1}.

Table 2 presents the reactions responsible for the formation of anionic and molecular products in aqueous solutions containing Cl^- and Br^- ions and the corresponding equilibrium constants.

Thus, the results of pulse radiolysis studies attest to an important role of admixtures of Br^- ions in the oxidation mechanism of the Cl^- ions. At an early radical ion step, in the presence of Br^- ions, the $Cl_2^{-\bullet}$ radical anions tend to be converted into $ClBr^{-\bullet}$ and $Br_2^{-\bullet}$. The subsequent decay of these species gives rise to a large number of molecular (Cl_2, ClBr, Br_2) and ionic (Cl_3^-, Cl_2Br^-, $ClBr_2^-$, Br_3^-) products which occur in equilibrium. It is noteworthy that this behaviour is caused by the fact that bromine is a weaker oxidant than chlorine. Therefore, it is reasonable to expect that iodine, whose oxidative properties are even less pronounced, would also tend to produce mixed radical anions and molecular products in the redox processes in aqueous solutions in the presence of Cl^- and Br^- ions.

6. The reactivity of $X_2^{-\bullet}$ radical anions

The $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $I_2^{-\bullet}$ radical anions behave as fairly strong oxidants. Table 3 lists the reduction potentials for these species and for halogen atoms (the values were taken from a paper by Stanbury,[37] who summarised the data on theoretical and experimental determination of the potentials of inorganic radicals). It can be seen that the oxidising properties of the radical anions and atoms diminish in the sequence Cl, Br, I. On passing from a halogen atom to the radical anion, the potential also decreases, which is due to complexing of the halogen atom by the halogen ion.

Table 3. Reduction potentials (E°) of some inorganic radicals.[37]

Pair	E° /V	Pair	E° /V
$Cl^\bullet/Cl^-$	2.41	$SO_4^{-\bullet}/SO_4^{2-}$	2.43
$Br^\bullet/Br^-$	1.92	$SO_3^{-\bullet}/SO_3^{2-}$	0.63
$I^\bullet/I^-$	1.33	$NO_3^\bullet/NO_3^-$	~2.5
$Cl_2^{-\bullet}/2\,Cl^-$	2.09	$CO_3^{-\bullet}/CO_3^{2-}$	~1.5
$Br_2^{-\bullet}/2\,Br^-$	1.62	$(CSN)_2^{-\bullet}/2\,CSN^-$	1.32
$I_2^{-\bullet}/2\,I^-$	1.03	$SeO_3^{-\bullet}/SeO_3^{2-}$	1.68

Note. The error of determination of the potential does not exceed ±(0.05–0.10) V.

A multitude of publications have been devoted to the reactivity of the $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$, and $I_2^{-\bullet}$ radical anions. This interest points to an important role of these species in the oxidation processes involving halogens. Selected values of the rate constants for the reactions of radical anions with some organic and inorganic ions and compounds in an aqueous solution are presented in Table 4. For most of reactions, the constants decrease in the sequence $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$, $I_2^{-\bullet}$ in parallel with weakening of the oxidising properties of radical anions. The rate constants for one-electron oxidation are, most often, rather high; however, they are substantially lower than those for the $OH^{\bullet}$ radicals,[9] which can be attributed to lower potentials of the $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ and $I_2^{-\bullet}$ radical anions compared to the potentials of $OH^{\bullet}$. Most of the constants given in Table 4 are lower than the values typical of diffusion-limited reactions. The rate of these reactions may be expected to depend substantially on the free energy [or the difference between the reduction potentials (ΔE°)] of the reacting species]. Indeed, for reactions of the same type between Np^{III} or Pu^{III} and $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ or $I_2^{-\bullet}$, one can follow the expected linear dependences of the logarithm of the rate constant on the ΔE°.[5] The review [5] describes in detail features of the kinetics and the mechanism of the reactions of halogen radical anions (and other inorganic radical anions) with actinides.

Table 4. Rate constants (k) for one-electron oxidation of a number of compounds by the $X_2^{-\bullet}$ radical anions [23, 38–50]

Compound	k /litre mol^{-1} s^{-1}		
	$Cl_2^{-\bullet}$	$Br_2^{-\bullet}$	$I_2^{-\bullet}$
$X_2^{-\bullet}$ (see [a])	2.2×10^9	2.2×10^9	3.2×10^9
Cr^{2+}	2.4×10^9	1.9×10^9	1.5×10^9
Fe^{2+}	1.4×10^7	3.6×10^6	3.6×10^6
NO_2^-	2.5×10^8	6.7	–
H_2O_2	1.4×10^5	$<1\times10^3$	–
U^{3+}	4.2×10^9	3.4×10^9	1.2×10^9
Ascorbic acid	6.0×10^8	1.1×10^8	$\leqslant6\times10^5$
Cysteine	8.5×10^8	1.8×10^8	–
$(CH_3)_2S$	3.0×10^9	3.2×10^9	–
4-Hydroxybenzoate	2.8×10^8	2.3×10^8	–
Tryptophan	2.6×10^9	7.0×10^8	$<1\times10^6$

[a] Recombination reaction: X = Cl, Br, I.

IV. Reactions of metal atoms and metal ions in unusual oxidation states

The hydrated electron and the hydrogen atom have high reduction potentials, whereas the $OH^{\bullet}$ radical, conversely, is an effective oxidant. Therefore, when these species react with metal ions, one-electron reduction or oxidation occurs provided that the ratio of the potentials meets the requirement of decreasing the free energy of the system. In the case of Pb^{2+} ions, both processes can take place

$$Pb^{2+} + e_{aq}^- \longrightarrow Pb^+,$$

$$Pb^{2+} + OH^{\bullet} \longrightarrow Pb^{3+} + OH^-.$$

This gives rise to Pb^{3+} and Pb^+ ions in unusual and unstable oxidation states; their electronic configurations are $d^{10}s^1$ and $d^{10}s^2p^1$, respectively. Due to the presence of one electron in the outer s or p orbital, this metal ion or atom is extremely reactive. These species can be compared to radicals having an unpaired electron. The lifetimes of these species in aqueous solutions are determined by kinetic factors and, as a rule, they are measured in micro- or milliseconds.

Many metals thermodynamically able to exist in water in unusual oxidation states have now been studied by pulse radiolysis. Data on the rate constants for the formation of metal ions in unusual oxidation states upon the reduction of stable metal ions with hydrated electrons and hydrogen atoms or their oxidation by means of $OH^{\bullet}$ radicals have been reported in the book.[9] The rate constants for some reactions involving metal atoms and ions in unusual and unstable oxidation states are documented.[51] The properties of these short-lived species are considered in most detail in reviews.[2, 3]

Table 5 presents characteristics of optical absorption and electrochemical potentials of metal atoms and ions in unusual oxidation states with the structure of aqua complexes. It can be seen that species with the electron configuration $d^{10}s^1$ exhibit one intense absorption band in the UV region. It was found [2, 3] that the energies of optical transitions in the absorption maxima ($E_{\lambda max}$) increase linearly with an increase in the ion charge (z). Within a Subgroup, the energy increases with an increase in the Period number. The pattern of optical absorption of the metal aqua complexes with other electronic configurations proves to be more complex. However, for metal ions with the electron configuration $d^{10}s^2p^1$, the longer-wavelength absorption band shifts to the UV region in the sequence Tl^0, Pb^+, Bi^{2+}, and the $E_{\lambda_{max}}$ value increases linearly with an increase in z, as for ions with the electron configuration $d^{10}s^1$.

Comparison of the potentials presented in Table 5 shows that copper, silver and gold atoms are effective reductants. This is due to the presence of one electron in their outer s orbitals. In isoelectronic series of metals, the potential tends to decrease with an increase in the charge of the metal ion. Within a single Subgroup (*i.e.*, for ions with the same charge), the potential increases with an increase in the Period number.

Metal atoms and metal ions in unusual oxidation states are highly reactive and, depending on the potential, they can either reduce or oxidise organic and inorganic compounds. The rate

Table 5. Optical characteristics and reduction potentials of metal atoms and aqua complexes of metal ions in unusual oxidation states (see the studies [1–3, 52–54] and references cited therein).

Metal	λ_{max} /nm	ε /litre mol^{-1} cm^{-1}	E° /V
Cu^0	380	5.6×10^3	−2.6
Cu^{3+}	265	1.1×10^3	~1.8
Zn^+	310	1.8×10^4	−2.3
Ga^{2+}	270	–	−0.63
Ag^0	360	1.6×10^4	−1.8
Ag^{2+}	275	5.4×10^3	–
Cd^0	240	2.0×10^4	−0.81
Cd^+	295	1.8×10^4	−1.8
In^0	500	$\geqslant1.8\times10^3$	−1.05
In^{2+}	250	2.0×10^4	−0.45
Sn^{3+}	~215	–	~0.7
Au^0	260	4.2×10^3	−1.5
Au^{II}	270,	6.3×10^4,	–
	440	2.0×10^3	–
Hg^0	254	2.8×10^3	0.68
Hg^+	250	1.4×10^4	−1.0
Tl^{2+}	~225	–	0.3
Tl^0	260,	9.0×10^3,	−1.9
	450	5.0×10^3	–
Pb^0	300	1.2×10^4	−0.96
Pb^{3+}	$\leqslant$210	–	1.8
Pb^+	320	2.5×10^3	~(−1.0)
Bi^{2+}	285	2.4×10^4	–
Mn^+	~300	–	–
Co^+	310,	4.4×10^3,	−1.8
	370	4.8×10^3	–
Ni^+	300	5.5×10^3	~(−2.7)
Ir^{II}	280	1.7×10^3	–
Pd^+	290	6.4×10^3	–

Table 6. Rate constants (k) for some reactions of metals in unusual oxidation states.[51]

Compound	k /litre mol^{-1} s^{-1}					
	Ag^0	Cr^{2+}	Zn^+	Ni^+	Cd^+	Co^+
O_2	5.0×10^9	1.6×10^8	–	2.2×10^9	1.0×10^{10}	3.2×10^9
H_2O_2	3.5×10^9	7.1×10^4	2.5×10^9	3.2×10^8	2.2×10^9	1.5×10^9
MnO_4^-	1.2×10^{10}	4.0×10^9	–	7.2×10^9	7.8×10^9	1.0×10^{10}
NO_3^-	–	–	2.1×10^9	1.4×10^6	3.5×10^8	1.8×10^9
BrO_3^-	–	–	2.1×10^9	–	1.3×10^8	–
CCl_4	1.1×10^9	–	–	–	–	$\leqslant6\times10^5$
$ClCH_2CO_2^-$	1.5×10^8	–	–	–	–	–
1,4-Benzoquinone	1.5×10^8	3.5×10^9	3.0×10^9	–	3.9×10^9	–

constants for some reactions involving metal atoms and ions in unusual oxidation states are summarised in Table 6. (This Table was compiled using data from the book.[51]) The reaction rate constants are usually fairly high; in some cases (for example, for reactions of Ag^0, Cd^+ and Co^+ with O_2, H_2O_2 and inorganic anions), they correspond to the diffusion limits. Apparently, the electron transfer occurs by an outer-sphere mechanism. Among the reactions not controlled by diffusion of the reactants, no reactions can be found for which the rate constant would follow a clear-cut dependence on the reduction potential of the metal ion.

Some metal atoms and metal ions in unusual oxidation states tend to add more metal ions to yield small clusters.[3,55–57] This ability is especially characteristic of atoms that can attach an additional metal cation with a σ_s-bond (Ag, Cu) or a σ_{sp}-bond (In, Tl), thus forming small homoelement clusters consisting of two to about ten atoms.[3,54–56] It was also found[58,59] that silver atoms, Ag_2^+ cations and, perhaps, Ag_3^{2+} cations form complexes with cyanide anions, ethylenediaminetetraacetic acid or ammonia. The optical properties, the redox potentials and the kinetic characteristics of such clusters differ appreciably from analogous properties of the clusters having a hydration shell. The nucleation processes of silver in polymeric membranes,[59–62] in gelatin[63] and on the surface of colloidal silica[64] follow similar mechanisms, *i.e.*, they include the intermediate formation of the same clusters as those formed in homogeneous aqueous solutions of silver ions, which have been described in detail in our review.[3]

The possibility of formation of short-lived mixed (heteroelement) clusters has also been established.[65–69] These arise upon the reactions of metal ions in unstable oxidation states, in particular Co^+ ion, with other metal ions in stable oxidation states, for example, with the Ag^+ ion. Under these conditions, a short-lived $(CdAg)^{2+}$ cluster is formed.[65,68] A similar approach has been used[66] to obtain mixed clusters, $(CdTl)^{2+}$, $(TlAg)^+$ and $(TlCd)^{2+}$.

A metal ion in an unusual oxidation state can not only react with a different metal ion to give a mixed cluster; it can also reduce or oxidise a different ion. For instance, Zn^+ ions obtained upon the reduction of Zn^{2+} with hydrated electrons, unlike Cd^+ ions, enter into electron transfer reactions with silver, thallium and cadmium ions, no mixed clusters being formed.[65,66,68] In addition, the Tl_2^+ ions reduce Pb^{2+} ions. By using metal ions with various reduction potentials and various electron structures, the conditions that favour one or another reaction were identified.[3] It was found that mixed clusters are formed in those cases where the potentials of reacting metal ions either coincide or do not differ much. This also requires the possibility of formation of a bonding molecular orbital between the atomic orbitals of the reacting metal ions. Fast electron transfer between metal ions takes place when the standard potentials of the ions are appreciably different.

V. Reactions of actinides

During recent years, a substantial contribution has been made to the study of the kinetics and mechanisms of one-electron redox reactions involving actinides. A specific feature of these elements is the diversity of stable oxidation states depending on the pH value and the presence of diverse ligands. The reduction of tetra-, penta-, hexa- and heptavalent actinides with hydrated electrons has very high rate constants ($\sim2\times10^9$ to 1×10^{11} litre mol^{-1} s^{-1}, see Refs. 70–78). As in the case of other diffusion-controlled one-electron redox reactions, no clear-cut correlation can be followed between the rate constants and the reduction potentials (E°) of the corresponding pairs of actinide ions. The rate constants for the reactions of actinides with hydrogen atoms which occur predominantly in acidic media are much lower (10^7–10^9 litre mol^{-1} s^{-1}).[79–81] This difference can hardly be explained by the fact that the reduction potential of a hydrogen atom (−2.3 V) is less negative than the potential of the electron (−2.87 V). The researchers cited attributed this to different reduction mechanisms. In the case of the hydrated electron, the reaction occurs as an outer-sphere electron transfer. The reaction of actinides with hydrogen is apparently an inner-sphere reaction, which includes the insertion of an H$^\bullet$ atom into the hydration shell to give the $H_3O^\bullet$ complex with subsequent transfer of an electron from this complex to the central ion. The logarithms of the rate constants for the reactions between a hydrogen atom and AnO_2^{2+} ions (An = U, Pu, Am, Np) were found to follow a nearly linear dependence on the reduction potential.[5] Thus, the mechanisms of reactions for them are identical and are not controlled by diffusion. Hydrogen atoms act as one-electron oxidants with respect to the U^V, Np^{III} and Pu^{III} ions. Apparently, this is due to the formation of hydride complexes of these actinides at an intermediate stage of the reaction.[80,82]

The rate constants for the actinide reactions with the OH$^\bullet$ radicals are 10^8–10^9 litre mol^{-1} s^{-1}, their values being markedly dependent on the acidity of the aqueous solution.[83–87] The reactions follow an inner-sphere mechanism involving either detachment of a hydrogen atom from a water molecule by the OH$^\bullet$ radical or the replacement of the OH^- ion in the hydration shell of the actinide ion by this radical.[5]

The oxidation of halide ions in aqueous solutions by hydroxyl radicals giving rise to the $X_2^{-\bullet}$ radical anions has been described above in detail. In aqueous solutions containing SO_4^{2-}, NO_3^- or CO_3^{2-} ions, similar processes give $SO_4^{-\bullet}$, $NO_3^\bullet$ or $CO_3^{-\bullet}$ radical anions, respectively. In recent years, systematic research of the kinetics and mechanism of one-electron redox reactions of actinides involving these species has been carried out. It was found that their reduction potentials are commensurate with the potential of the OH$^\bullet$ radical in the pH region of 1–13 and they tend to oxidise actinides. Moreover, the rate constants for the $SO_4^{-\bullet}$ radical anion,[81,84] $NO_3^\bullet$ radical[84,88,89] and $CO_3^{-\bullet}$ radical anion[77,87] usually do not differ much from those for the OH$^\bullet$ radical. In the case of noncharged $NO_3^\bullet$ radical, the reaction rates are most likely controlled by diffusion, as for the $HSeO_3^\bullet$ radical.[90]. The rate constants for the reactions of Np^V and Np^{VI} with the ozonide $O_3^{-\bullet}$ radical anions are as low as 2×10^6 and 2×10^5 litre mol^{-1} s^{-1}, respectively.[91]

The reactions with halogen radical anions usually have lower rate constants than the reactions with sulfate and nitrate radicals.[84,88,89,92–94] As has already been noted, for the reactions of Np^{III} or Pu^{III} with $Cl_2^{-\bullet}$, $Br_2^{-\bullet}$ or $I_2^{-\bullet}$, the logarithm of the rate constant obeys a linear dependence on the difference between the reduction potentials (ΔE°) of the reacting species. Similar correlations can be followed for reactions of $CO_3^{-\bullet}$ with the carbonate complexes of Am^{III}, Np^{III} and Pu^{III} (see Ref. 77) or U^V, Np^V and Pu^V (see Ref. 95). Thus, if the reaction rate is not controlled by diffusion, it often depends on the reduction potentials of actinide ions and the inorganic radicals they react with. For example, the

reactivity in redox processes decreases in the following sequence: $SO_4^{-\bullet} > NO_3^{\bullet} > OH^{\bullet} > Br_2^{-\bullet} > Cl_2^{-\bullet} > I_2^{-\bullet} > O_3^{-\bullet}$ (see Ref. 5). The reactivity of actinides towards the $OH^{\bullet}$ radical and the inorganic radical anions listed above is appreciably affected by their charge and complexation state. This is due to the inner-sphere mechanism of the reactions involved.

Reactions of actinides with organic radicals are discussed in the following Section.

VI. Reactions of organic radicals

A large body of experimental data (mainly obtained by pulse radiolysis) concerned with the reactivity of organic radicals towards the one-electron reduction of organic and inorganic compounds in aqueous solutions has been accumulated to date. The measured rate constants have been summarised in a book.[96] Table 7 presents the rate constants for the reduction of a number of organic and inorganic compounds with various organic radicals and with hydrogen atoms. These particular constants were chosen [97–103] among the multitude of known rate constants because they allow one to follow the requlrities of their variation in a series of related organic radicals. These are 1-hydroxyalkyl radicals formed upon pulse radiolysis of aqueous solutions of alcohols in reactions of type (3). It is reasonable to expect that the reactivity of organic radicals in the one-electron reduction of organic and inorganic compounds should depend, most of all, on the reaction mechanism and limiting step. The reduction potential of the hydrogen atom is −2.3 V; the rate constants for the reductions involving the hydrogen atom are usually very high and are restricted by the rate of diffusion. In the case of organic radicals, the constants are also fairly high,[96] but they are still markedly lower than those for hydrogen. The rate constants for a large number of redox reactions involving organic radicals, including alkyl radicals ($^{\bullet}CH_3$, $CH_3C^{\bullet}H_2$, *etc.*) formed upon abstraction of a hydrogen atom from the α- or β-position of mono- or polyhydric alcohols, amines, nitro derivatives and other organic compounds, have now been measured. Most of these species react at high rates (10^6–10^9 litre mol^{-1} s^{-1}) with organic and inorganic compounds, mainly as reducing agents. The reduction of nitro, sulfo and halogen compounds and other organic compounds containing electronegative substituents and the reduction of various quinones, dyes, and their derivatives proceed at high rates, their rate constants reaching the values normally observed for diffusion-controlled reactions. Unfortunately, the reduction potentials of organic radicals are not always known, which restricts the possibility of comparison of rate constants and hampers elucidation of the reaction kinetics. However, the potentials of 1-hydroxyalkyl radicals $^{\bullet}CH_2OH$, $CH_3C^{\bullet}HOH$ and $(CH_3)_2C^{\bullet}OH$ have been determined; they decrease along the given series as follows: −1.18, −1.25 and −1.39 V.[8] Thus, the reducing ability of the radicals is enhanced in this sequence. It appeared of interest to find the relationship between the reactivity and the reducing capacity and the size of the radicals. Analysis of the reactivity (see Table 7) showed that the rate constants for the reactions of 1-hydroxyalkyl radicals with metal ions (Cu^{2+} and Cr^{2+}) decrease, while those for reactions with organic compounds (nitrobenzene, RNO, PNAF and NF), conversely, increase in the sequence $^{\bullet}CH_2OH$, $CH_3C^{\bullet}HOH$, $(CH_3)_2C^{\bullet}OH$. It is worth mentioning that for some other compounds,[96] it is not always possible to distinguish a clear-cut regularity in the variation of the constant as a function of the potential or the size of the radical. It should be borne in mind that determination of the rate constants of reactions involving organic radicals by pulse radiolysis with optical recording is faced with some experimental difficulties, which are caused by the following reasons. Organic radicals absorb in the far UV region and the extinction coefficients are relatively low. This hampers the measurement of the rate constants of reactions involving such radicals directly by following their absorption. The rate of appearance of the absorption of the reaction product is not always measurable. Therefore, many constants have not been determined by the direct method but were found by comparing the reactivity of the compound under study with a known reactivity of a different compound, the product of whose reduction has optical characteristics suitable for the measurements. These difficulties have been taken into account by Ershov *et al.*[104–106] They performed a systematic pulse radiolysis study of the reactivity of hydrogen atoms and a series of 1-hydroxyalkyl radicals $^{\bullet}CH_2OH$, $CH_3C^{\bullet}HOH$ and $(CH_3)_2C^{\bullet}OH$ towards the reduction of Hg^{2+} ions and I_2 molecules. These radicals differ in size and in the values of known redox potentials. The reagents (Hg^{2+} and I_2) differ appreciably in the outer-sphere and electronic structures. Therefore, different reduction mechanisms could be expected. The products of reduction of the radical acceptors (Hg^{+} and $I_2^{-\bullet}$) have appropriate optical characteristics which allow the rate constants of these reactions to be measured with high accuracy.

The reactions were carried out in acidic (pH 1.0–2.0, $HClO_4$) aqueous solutions of $Hg(ClO_4)_2$ and I_2 containing small amounts of an alcohol (methanol, ethanol or 2-propanol). Under these conditions, hydrated electrons reacted with H^+ to give hydrogen atoms

$$e_{aq}^- + H^+ \longrightarrow H^{\bullet}. \quad (32)$$

The hydrogen atoms, like $OH^{\bullet}$ radicals, entered into a reaction of type (3) with alcohols, which were thus converted almost entirely into alcohol radicals ($R^{\bullet}$).

Then the alcohol radicals reacted with the Hg^{2+} ions or I_2 molecules:

$$R^{\bullet} + Hg^{2+} \longrightarrow Hg^{+} + X + H^{+}, \quad (33)$$

$$R^{\bullet} + I_2 \longrightarrow I_2^{-\bullet} + X + H^{+}, \quad (34)$$

where X is CH_2O, CH_3CHO and $(CH_3)_2CO$ in the case of CH_3OH, CH_3CH_2OH and $(CH_3)_2CHOH$, respectively.

The rate of the reaction of the alcohol radicals with the Hg^{2+} ions was measured based on the appearance of absorption bands with maxima at $\lambda = 225$ and 255 nm corresponding to the Hg^{+} ion formed in reaction (33).[107, 108] The reaction with I_2 was monitored by following the absorption at $\lambda = 725$ nm due to the the $I_2^{-\bullet}$ radical anion produced in reaction (34).[109, 110]

Table 7. Rate constants (k) for some reactions involving hydrogen atoms and organic radicals.

Atom, radical	E°/V	k /litre mol^{-1} s^{-1}							
		Hg^{2+} (see [103]) (pH 2)	Cu^{2+} (see [95, 96]) (pH 5–6)	Cr^{2+} (see [97]) (pH 1)	I_2 (see [104–106])	RNO (see [98])	NF (see [99])	PNAF (see [100])	$C_6H_5NO_2$ (see [101])
$H^{\bullet}$	−2.30	2.0×10^9	–	–	3.5×10^{10}	–	–	–	–
$^{\bullet}CH_2OH$	−1.18	7.0×10^8	1.6×10^8	1.6×10^8	5.0×10^9	7.9×10^8	8.0×10^8	1.0×10^8	3.2×10^9
$CH_3C^{\bullet}HOH$	−1.25	3.8×10^8	9.0×10^7	7.9×10^7	6.5×10^9	2.4×10^9	1.5×10^9	8.0×10^8	3.9×10^9
$(CH_3)_2C^{\bullet}OH$	−1.39	3.1×10^8	5.0×10^7	5.1×10^7	8.0×10^9	3.2×10^9	3.3×10^9	3.8×10^9	5.0×10^9

Note. RNO is *N*,*N*-dimethyl-4-nitrosoaniline; NF is *anti*-5-nitro-2-furaldoxime; PNAF is *p*-nitroacetophenone.

The data on the formation of the Hg^+ cation were analysed in terms of the reaction scheme composed of the following reactions with known rate constants:[9,96]

$$R^\bullet + R^\bullet \longrightarrow \text{product},$$

$$H^\bullet + H^\bullet \longrightarrow H_2,$$

$$Hg^+ + Hg^+ \longrightarrow Hg^0 + Hg^{2+},$$

$$H^\bullet + Hg^{2+} \longrightarrow Hg^+ + H^+.$$

The rate constants for the recombination of alcohol radicals are 2.4×10^9, 1.5×10^9 and 1.1×10^9 litre mol^{-1} s^{-1} for $^\bullet CH_2OH$, $CH_3C^\bullet HOH$ and $(CH_3)_2C^\bullet OH$, respectively.[111] Computer simulation gave the following rate constants for reaction (33) with the $^\bullet CH_2OH$, $CH_3C^\bullet HOH$ and $(CH_3)_2C^\bullet OH$ radicals: 7.0×10^8, 3.8×10^8 and 3.1×10^8 litre mol^{-1} s^{-1}, respectively. Thus, the rate constants for the reactions of the alcohol radicals with the Hg^{2+} ions decrease in the above sequence.

A similar approach has been used to calculate the rate constants for reactions (34) between the alcohol radicals and I_2 on the basis of the kinetics of the appearance of $I_2^{-\bullet}$ absorption. The following reactions were taken into account:

$$H^\bullet + I_2 \longrightarrow I_2^{-\bullet} + H^+,$$

$$I_2^{-\bullet} + I_2^{-\bullet} \longrightarrow I_3^- + I^-,$$

$$I^\bullet + I^- \rightleftharpoons I_2^{-\bullet},$$

$$I_2 + I^- \rightleftharpoons I_3^-,$$

$$I^\bullet + I^\bullet \longrightarrow I_2.$$

In this case, the rate constants for the forward and back reactions and the extinction coefficients of the reactants and the products are known.[109,110] The rate constants for the reduction of iodine in reaction (34) by the $^\bullet CH_2OH$, $CH_3C^\bullet HOH$ and $(CH_3)_2C^\bullet OH$ radicals are 5.0×10^9, 6.5×10^9 and 8.0×10^9 litre mol^{-1} s^{-1}, respectively. Thus, the rate constants for the reactions of alcohol radicals with I_2, unlike reactions with Hg^{2+}, increase in this sequence. It is also noteworthy that an increase in the values of constants with an increase in the size of the radical definitely indicates that the reactions involving these radicals are not controlled by diffusion.

The rate constants for the alcohol radicals and hydrogen atoms with I_2 increase with an increase in the reduction potentials (see Table 7). Moreover, a good linear dependence of $\log k$ on the reduction potential of the reagent can be followed (Fig. 3 *a*). Therefore, it can be concluded that the efficiency of the outer-sphere transfer of an electron from the alcohol radicals to the I_2 molecule is determined by their reducing capacity. It is of interest that the hydrogen atom fits well in this series of radicals as regards the reduction mechanism and the variation in the potential.

The rate constants for reactions of the Hg^{2+} ions with the hydrogen atoms and alcohol radicals increase with a decrease in the size of the reducing agent (see Table 7). Therefore, it can be suggested that the reaction of the radicals $R^\bullet$ with Hg^{2+} gives initially the short-lived $[Hg^{2+} \cdots R^\bullet]$ complex; this is followed by an inner-sphere electron transfer and separation of the reaction products. Note that the formation of relatively stable complexes in similar reactions is typical of many metals, most often, transition metals.[2,3] Due to steric hindrance, which becomes more pronounced with an increase in the size of the radical, the rate of formation of the intermediate complex should limit the rate of reduction; this is actually observed in experiments. The tendency of transition metals to form unstable hydride complexes upon reactions with hydrogen atoms has been confirmed experimentally in some cases.[1,2,53] It is also assumed that the reactions of hydrogen atoms proceed with participation of water present in the hydration shell of the ion; this may give intermediately the $H_3O^\bullet$ species, an electron from which passes to the central metal ion.

The conclusions drawn from the study of the reactivity of alcohol radicals with respect to the Hg^{2+} ion and with I_2 can be extended to the reactions of these radicals with other metals and compounds (see Table 7). Indeed, for the Cu^{2+} and Cr^{2+} ions, as for Hg^{2+}, the rate constants for reactions with alcohol radicals regularly decrease in the sequence $^\bullet CH_2OH$, $CH_3C^\bullet HOH$ and $(CH_3)_2C^\bullet OH$, which can also be attributed to the steric hindrance involved in the reactant interaction. Conversely, in the reactions with organic compounds (nitro- and nitrosobenzene, RNO and NF), the rate constants increase in the given sequence (see Table 7). This is due to the fact that the efficiency of the electron transfer to a molecule of the organic compound is determined by the reduction potential of the radical. In this case, as in the case of iodine, the logarithm of the rate constant follows a linear dependence on the potential (see Fig. 3 *b*).

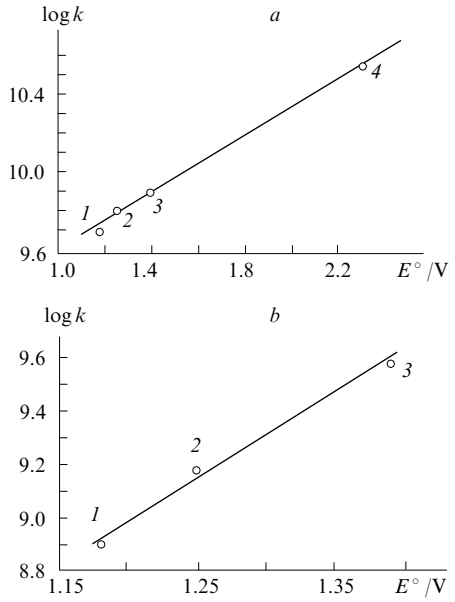


Figure 3. Dependence of $\log k$ on the potential (E°) in the reactions of $^\bullet CH_2OH$ (*1*), $CH_3C^\bullet HOH$ (*2*) and $(CH_3)_2C^\bullet OH$ (*3*) radicals and hydrogen atom (*4*) with I_2 (*a*) and with *N*,*N*-dimethyl-4-nitrosoaniline (*b*).

However, the conclusion concerning the inner-sphere mechanism of the reduction of transition metal ions, Hg^{2+}, Cu^{2+} and Cr^{2+}, with organic radicals is not universal and it cannot be extended to all other ions. For example, the alcohol radicals reduce the Fe^{3+} cations, their reactivity increasing in the sequence $^\bullet CH_2OH$, $CH_3C^\bullet HOH$ and $(CH_3)_2C^\bullet OH$ ($k = 8 \times 10^7$, 3.8×10^8 and 5.8×10^8 litre mol^{-1} s^{-1}, respectively).[96] This fact rather attests in favour of a mechanism with outer-sphere electron transfer in which the reducing properties of the radical are of crucial importance. Note that reactions of the alcohol and many other organic radicals with transition metal complexes [$Fe(CN)_6^{3-}$, $IrCl_6^{2-}$, *etc.*] are diffusion-controlled, the rate constants reaching $\sim 5 \times 10^9$ litre mol^{-1} s^{-1} and depending only slightly on the type of the reducing radical used.[96]

The rates of reactions of organic radicals with oxygen are also controlled by diffusion; they are characterised by constants of $\sim 10^9 - 10^{10}$ litre mol^{-1} s^{-1}. These reactions yield the $RO_2^\bullet$ radicals or the $O_2^{-\bullet}$ peroxide radicals. Conversely, the reactions with H_2O_2 are very slow ($\sim 1 \times 10^5$ litre mol^{-1} s^{-1}) and seem to be accompanied by the formation of the $OH^\bullet$ radicals.

The reactions of the $CO_2^{-\bullet}$ radical anion with various inorganic and organic compounds have been studied in detail. The reduction potential of this radical anion is -1.9 V; as a reducing agent, it markedly surpasses other radicals, being inferior only to the hydrated electron and the hydrogen atom. Therefore, this species tends to enter into electron transfer reactions with various compounds and the rate constants of such reactions approach the diffusion limit.[96]

Comparison of the reduction potentials of metal ions in unusual oxidation states and organic radicals (see Tables 5 and 7) shows that some metal ions, for example, Zn^+, Cd^+, *etc*., surpass organic radicals in reducing ability. Therefore, in those radiation-induced chemical reactions where they arise simultaneously [for example, in the reduction of metal ions, Zn^{2+}, Cd^{2+}, *etc*., by hydrated electrons or in dehydrogenation of organic compounds by reaction (3)], organic radicals are reduced by metal ions. Conversely, for higher potentials of metal ions (for ions like Pb^+, Hg^+ and, probably, Pd^+ and Pt^+), the radicals reduce the ions to give metal atoms.

In the studied reactions of actinides with organic radicals, the latter behave as reducing agents.[5,112–115] It is noteworthy that data on the reactivity of organic radicals towards actinides and on the nature of the products are important for evaluation of the radiation stability of organic extractants used in the radiochemical industry and for predicting the efficiency of actinide separation. According to publications,[112–115] the rates of the reactions of the $^{\bullet}COOH$ and $(CH_3)_2C^{\bullet}OH$ radicals and *o*-phenanthrolinium, 2,2′-bipyridinium and some other electron adducts with actinide ions can be fairly high and, most likely, they are controlled by diffusion. This is supported by calculation of the diffusion-limited rate constant for the reaction of Np^{VI} with $(CH_3)_2C^{\bullet}OH$ using the Smolukhovsky equation.[115] The value calculated theoretically proved to be rather close to the experimental value. In addition, it was found that the activation energies for the reaction of U^{VI} with the *o*-phenanthrolinium and 2,2′-bipyridinium electron adducts are equal to 10 and 16.7 kJ mol^{-1}, respectively. These values do not differ much from the activation energy of water diffusion and are usual for reactions whose rates are controlled by diffusion or approach the diffusion limit.

It is worth mentioning that the electronic structure of organic radicals has a considerable influence on the rates of their reactions with actinides. It was found [116] that reactions of uranium, neptunium, plutonium and americium ions with the *o*-phenanthrolinium and 2,2′-bipyridinium H-adducts proceed much more slowly than reactions with the electron adducts of the same compounds. This is attributable to the fact that the electron adduct arises upon protonation of the nitrogen atoms in the molecules, whereas the H-adduct is produced upon incorporation of the hydrogen atom into the aromatic rings. Therefore, in the electron adducts, the unpaired electron is delocalised over the aromatic π-system, whereas in the H-adducts, the system of conjugation is violated due to the formation of a cyclodienyl type radical. The electron transfer proceeds more easily from the electron adduct than from the H-adduct due to the difference between their electronic structures.

Thus, it can be concluded that, at least for some reduction reactions involving organic radicals, the redox process follows a classical pattern, according to which the reaction proceeds either in the outer or in the inner sphere. For the former type, the interaction between the oxidant and the reductant is not significant during the electron transfer and, most likely, it does not affect the coordination spheres of the reactants. As has been shown, for these reactions, a clear-cut dependence of the reactivity of organic radicals on their reducing potential can be observed. A necessary condition for reactions of the latter type is the presence of a strong bond between the reductant and the oxidant during the electron transfer, which is implemented by the formation of a short-lived intermediate complex. In this case, the rate of electron transfer is limited by this step and depends more appreciably on steric factors.

VII. Conclusion

The results of investigation of a number of redox reactions in aqueous solutions initiated by exposure to ionising radiation indicate that development of this line of research is quite promising. The pulse radiolysis method provides broad opportunities for the study of the kinetics, the mechanism and the nature of the short-lived intermediates of fast one-electron redox reactions. By the early 1990s, a great amount of information had been accumulated on the reactivity of hydrated electrons, hydrogen atoms, hydroxyl radicals and $HO_2^{\bullet}$ radicals,[8] diverse inorganic [23] and organic [96] radicals, metal ions in unusual oxidation states [51] and actinides.[5] During the last 15 years, new data have been obtained, which are largely summarised in this review. Of these, mention should be made first of all of the studies of the redox processes involving halide ions. The rate and equilibrium constants for many reactions have been measured for the first time and the tendency of halogens for the formation of mixed products of not only molecular but also radical nature has been established. The $ClBr^{-\bullet}$ radical anion is probably only the first representative of this series. The research along these lines, important from not only a theoretical but also a practical standpoint, will undoubtedly be continued.

In our opinion, the theoretical analysis of the data on the reactivity of diverse one-electron oxidants and reductants of radical nature towards various compounds still receives inadequate attention. Systematic analysis of these data would be useful for the development of chemical kinetics and for extension of the knowledge on the mechanisms of chemical reactions.

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