

PHYSICAL CHEMISTRY
OF SOLUTIONS

Primary Stage of the Reaction between Ozone and Chloride Ions in Aqueous Solution: Can Chloride Ion Oxidation by Ozone Proceed via Electron Transfer Mechanism?

A. V. Levanov, E. E. Antipenko, and V. V. Lunin

Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia

e-mail: levanov@kge.msu.ru

Received April 28, 2011

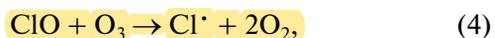
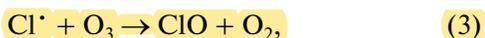
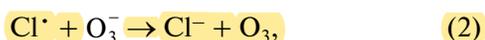
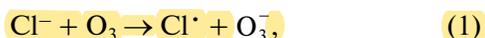
Abstract—It is found that chloride-ion oxidation by ozone via electron transfer mechanism does not occur due to its extremely high endoergicity and negligibly low rate. It is concluded that all processes supposedly associated with this reaction, particularly ozone decomposition in sodium chloride solution initiated by Cl^\cdot atoms, do not take place either. It is shown that experimental data on the products and kinetic regularities of the interaction of O_3 with Cl^- contradict the assumption that the electron transfer reaction is its primary stage. In fact, chloride-ion oxidation by ozone proceeds via the mechanism of oxygen atom transfer. It is noted that in order to estimate the possibility of using an ozonated physiological saline in medicine, the formation of chloride-ion oxidation products and ozonation byproducts must be taken into account.

Keywords: ozone, chloride-ion, electron transfer reaction, physiological saline, chemical reaction kinetics.

DOI: 10.1134/S0036024412040164

INTRODUCTION

It was shown in [1] that the primary stage of ozone reaction with chloride-ion proceeds via the mechanism of oxygen atom transfer. This agrees with all experimental data (the composition of the products, kinetic regularities, etc.) known about the process and clarifies them. The present work is devoted to analyzing the assumption that the primary stage of the interaction of O_3 with $\text{Cl}^-(\text{aq})$ is a process of electron transfer from chloride-ion to O_3 molecule. This hypothesis was presented in [2, 3] and it is based on the observation that, in investigating ozone interaction with sodium chloride solution, the authors of [2, 3] could not detect the products of chloride-ion oxidation. Meanwhile, the rate of O_3 decomposition increased in comparison to pure water [2, 3]. According to [2, 3], the process of ozone decomposition in chloride-ion solutions can in general be described by the following scheme:



its primary stage being the oxidation of chloride-ion by ozone via the electron transfer mechanism.

First of all, let us estimate the rates of direct reaction (1), using the classical variant of Marcus theory of

electron transfer reactions [4, 5]. According to Marcus, the Gibbs energy of activation of an electron transfer reaction is

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^\circ}{\lambda} \right)^2, \quad (5)$$

where ΔG° is standard Gibbs energy of the reaction, and λ is the parameter called reorganization energy. The general expression for the energy of activation ΔG^* contains additional terms [5]; for reaction (1), however, they either vanish due to the reaction proceeding between one charged and one uncharged particle, or are negligibly small as the reaction takes place in water—a solvent with high dielectric permeability.

The Gibbs energy of reaction (1) $\Delta_1 G_{298}^\circ$ is calculated from the values of Gibbs energy of formation of its participants in aqueous solution (see [6, 7] and Appendix). $\Delta_1 G_{298}^\circ = 127$ kJ/mol is obtained. The corresponding equilibrium constant value is $K_{1,298} = 5.8 \times 10^{-23}$; i.e., the equilibrium of reaction (1) is completely shifted toward primary substances.

Estimates of reorganization energy λ_1 for reaction (1) and the corresponding rate constants are given in Appendix. It should be noted that, according to (5), the least value of Gibbs energy of activation for electron transfer reaction is $\Delta G_{\min}^* = \Delta G^\circ$ if $\lambda = \Delta G^\circ$. We therefore use below the estimate $\Delta_1 G^* > \Delta_1 G_{298}^\circ = 127$ kJ/mol for the Gibbs energy of activation of reaction (1) in order to avoid any doubts as to the correctness of our

estimates of λ_1 . This will allow us to calculate the upper limit (the highest possible value) of the rate constant of reaction (1).

Based on reference values of electron affinity for a chlorine atom (3.6127 eV) and ozone molecule (2.1028 eV) [8], we can calculate the value of enthalpy for reaction (1) in gas phase, $\Delta_1 H_0^\circ = 1.511 \text{ eV} = 146 \text{ kJ/mol}$, which is in satisfactory agreement with the estimate $\Delta_1 G^* > 127 \text{ kJ/mol}$ for reaction (1) in solution.

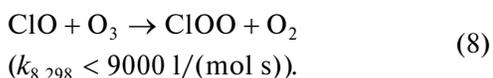
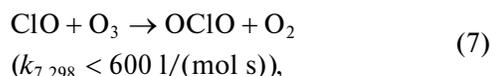
According to Marcus [4, 5], the value ΔG^* is identified with the energy of activation, and the rate constant of electron transfer is estimated using the formula

$$k = Z \exp(-\Delta G^*/RT), \quad (6)$$

where Z is the frequency of collision. The value of $Z \sim 1.2 \times 10^{10} \text{ l/(mol s)}$ was calculated from Smolukhovskii's equation for the frequency of diffusion controlled collisions in aqueous solution at 25°C. Formula (6) can predict considerably overestimated values of the real constant, as it assumes that each collision with sufficient energy gives rise to a reaction. From formula (6), we obtain the rate constant of reaction (1) at 25°C $k_1 < 7 \times 10^{-13} \text{ l/(mol s)}$. Such a low rate constant value means that neither primary reaction (1) nor any secondary reactions in which products of reaction (1) would participate occur in reality.

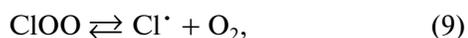
The authors of [2, 3] believed that the chlorine atoms formed in reaction (1) (though in very low concentration) cause the chain reaction of ozone decomposition (3), (4). In our opinion, the ozone decomposition scheme (1)–(4) ignores a number of very important factors.

First, elementary reaction (4) does not exist. Such a reaction was postulated in some earlier works devoted to the interaction of chlorine and ozone. According to modern concepts (see, e.g., [9]), ClO interacts relatively slowly with ozone in the gas phase via the reactions



Reaction (7) does not lead to chain propagation; the forming chlorine dioxide OClO is further oxidized by ozone to chlorine trioxide ClO₃. In aqueous solutions, the final products of interaction between chlorine dioxide and ozone are chlorate-ion and low quantities of perchlorate [10, 11].

The radical ClOO formed in reaction (8) exists in the gas phase in equilibrium with the products of its decomposition [12],



equilibrium (9) being shifted toward the formation of Cl[·] atoms ($\Delta_9 G_{298}^\circ = -7 \text{ kJ/mol}$, according to [13]). It

might be supposed that regeneration of Cl[·] atoms, which are necessary for propagation of the chain reaction of ozone decomposition (3) and (4), proceeds via reactions (8), (9). In contrast to scheme (1)–(4), however, the reverse transformation of ClO into Cl[·] atom is only partial, this process being quite slow. The remaining ClO is oxidized by ozone and does not participate in the propagation of the chain reaction. A high chemical activity of ClO and the possibility of its rapid interaction with ozone was substantiated in [2] by references to [14, 15]. However, just the opposite was noted in these papers: the reaction of ClO with O₃ is slow and may be ignored.

Second, ozonide-ion O₃⁻, the formation of which is assumed at stage (1), is a very active particle. If reaction (1) occurred in reality, it would be necessary to consider reactions of O₃⁻ in the suggested scheme. This was mentioned in [2, 3], but reactions of O₃⁻ were not considered.

Third, the suggested scheme fails to consider that in aqueous solutions containing chloride-ions, chlorine atoms react very rapidly with Cl⁻, forming the stable radical anion Cl₂⁻:



The constant of equilibrium (10) is $1.4 \times 10^5 \text{ l/mol}$, and the rate constant of direct reaction (10) is $8.5 \times 10^9 \text{ l/(mol s)}$ [16]. Such high values of the constants show that there are virtually no free chlorine atoms in a solution. Thus, in order to account for the specificity of the reactions in aqueous solutions containing chloride-ions, reactions of radical anion Cl₂⁻ should be considered instead of those for Cl[·] atoms. The Cl₂⁻ anion radical interacts with ozone (rate constant, $9 \times 10^7 \text{ l/(mol s)}$ [17]), the product of this reaction being (perhaps) ClO.

Fourth, the recombination reactions of active particles (Cl₂⁻, Cl[·], ClO, etc.) are not considered in the suggested scheme. In aqueous solutions, these reactions proceed at very high rates approaching the diffusion limit (see, e.g., [16]), causing a considerable drop in the concentrations of active particles. This should lead to a substantial reduction in the ozone decomposition rate via scheme (1)–(4).

Let us obtain a numerical estimate of the ozone decomposition rate according to scheme (1)–(4). Keeping in mind all of the above, the scheme should be augmented with the reaction between ClO and O₃ (7), leading to no chain propagation. Also, the decay of the ozonide ion due to its high chemical activity should be taken into account. The disappearance of O₃⁻ is described by means of an effective process:



In all other respects, there are no deviations from the original version of scheme (1)–(4). We therefore accept the assumption that the reactions proceed with the participation of a free chlorine atom, and the recombination reactions of active particles are not considered. It is assumed that all stages of the scheme except direct reaction (1) are so fast that the steady-state approximation for concentrations of Cl^\cdot , ClO , and O_3^- is fulfilled. For Cl^\cdot and ClO , this is due to the assumptions made in [2, 3], while for O_3^- it follows from its high chemical activity. The accepted assumptions lead to overestimation of ozone decomposition rate.

An analysis of schemes (1)–(4), (7), (11) by means of steady-state approximation, with allowance for the decay rate of the ozonide ion in effective process (11) being much higher than the rate of its decay via reverse reaction (2), leads to the following expression for the ozone decomposition rate:

$$-d[\text{O}_3]/dt = k_1(3 + 2k_3/k_7)[\text{Cl}^-][\text{O}_3].$$

The effective rate constant of ozone decomposition in an aqueous solution containing chloride-ions is determined by the relation

$$k_{\text{O}_3} = k_1(3 + 2k_3/k_7)[\text{Cl}^-]. \quad (12)$$

It is assumed that the constant ratio k_3/k_7 for reactions (3) and (7) in solution is the same as the constant ratio k_8/k_7 for reactions (8) and (7) in the gas phase; then $k_3/k_7 = 15$. This ratio should in fact be lower, since only part of the ClOO (the product of reaction (8)) can be transformed into chlorine atoms. From the above estimate $k_1 < 7 \times 10^{-13} \text{ l}/(\text{mol s})$, we find (according to (12)) that the effective rate constant of ozone decomposition in a 0.15 M solution of NaCl is $k_{\text{O}_3} < 3 \times 10^{-12} \text{ s}^{-1}$, corresponding to a half-life of >6500 years. The rate constant k_{O_3} value is so insignificant that ozone decomposition initiated by reaction (1) does not occur under any conditions. It should be noted that all assumptions made in estimating the rate of direct reaction (1) and analyzing scheme (1)–(4), (7), (11), lead only to overestimation of the rate constant k_1 and ozone decomposition rate; the real magnitudes of these values should be even lower than those obtained in the present work.

The statement that the primary stage of interaction of Cl^- with ozone is oxidation of Cl^- via the mechanism of electron transfer from chloride-ion to ozone molecule is based on the observation that, according to [2, 3], "...ozone decomposition in aqueous solutions of NaCl is not accompanied by the formation of any products except oxygen; in particular, there are no hypochlorites or chlorates in any noticeable amounts..." [2]. In fact, ozone participates in chemical reactions with ozone in aqueous solutions, with products of chloride-ion oxidation being formed as a result of the reaction (cf., e.g., references in [1]). The

question arises as to why the authors of [2, 3] failed to detect any products of chloride-ion oxidation by ozone.

Attempts were made in [2, 3] to determine the volume of hypochlorite-ion ClO^- in a reaction solution by a direct spectrophotometry. However, it is known (and was mentioned in [2] as well) that hypochlorite interacts with ozone quite rapidly, much faster than chloride ions do [18, 19]. In the process of ozonation of 9 g/l = 0.15 M solution of NaCl, hypochlorite concentration does not exceed 2 μM (it is easy to obtain this estimate from the rate constants for reactions of hypochlorite formation and consumption [18–21]). The absorption spectrum of hypochlorite in aqueous solution is of low intensity ($\lambda_{\text{max}} = 290 \text{ nm}$, $\epsilon_{290} = 350 \text{ l}/(\text{mol cm})$ [22]). Moreover, the band of hypochlorite overlaps with the shoulder of a very intense band of ozone ($\lambda_{\text{max}} = 254 \text{ nm}$, $\epsilon_{254} \sim 3000 \text{ l}/(\text{mol cm})$ [23, 24]). It is clearly not manageable to determine hypochlorite by spectrophotometry under these conditions.

Furthermore, the pH value of the reaction solution is not known (a value of pH 6.3 is indicated only in the captions to Figs. 1 and 3 in [2], where the results of a different experiment are presented). However, the products of ozone's reaction with chloride ions can be different substances (Cl_2 , or HOCl^\cdot , or ClO_3^-), depending on the pH. If the experiments under consideration were performed at pH 6.3, hypochloric acid would be the main interaction product. It has a band of low intensity in the UV spectrum ($\lambda_{\text{max}} = 235 \text{ nm}$, $\epsilon_{235} = 100 \text{ l}/(\text{mol cm})$ [22]), which is in the overlap range of the intense signals of ozone and chloride ions (see Fig. 2 in [2]). Direct spectrophotometry is therefore not suitable for the determination of HOCl either.

An attempt was also made in [2] to detect chlorates from the weight gain of dry residue after vacuum water distillation off a solution in which chloride ions and ozone were interacting (the pH of the solution was not indicated). If the pH of the reaction solution was 6.3, hypochloric acid HOCl would have been the main reaction product (together with some fraction of ClO_3^-), which had to escape during vacuum distillation.

Thus, due to a number of preventing factors, the sensitivity of analytical methods used in [2, 3] was not sufficient for determination of the targeted substances. It is interesting to compare [2] and [25], in which experiments on the ozonation of an aqueous solution of pure sodium chloride were also performed. The experimental procedures in both papers were almost identical. In contrast to [2], however, a sensitive iodimetric method for the determination of products was used in [25]. As a result, the formation of products of chloride-ion oxidation (hypochloric acid HOCl) during O_3 interaction with NaCl solution was revealed in [25], and the concentration of HOCl rose steadily over time.

The investigations in [2, 3] were performed mainly with the aim of substantiating the possibility of using ozonated physiological salines in medical practice. In this respect, it is important to emphasize that the products of chloride-ion oxidation by ozone could have harmful effects on the human organism. It was found in [11, 26, 27] that the main nonvolatile product of ozone interaction with chloride ions in neutral and alkaline solutions is the chlorate ion ClO_3^- . The primary toxic effect of chlorate is the oxidative destruction of erythrocytes [28]. It is quite possible that chlorate forms in low concentrations during the ozonation of physiological salines. As a preparation for injections into human blood, however, the acceptable chlorate level should also be quite low. In potable water, acceptable chlorate concentrations must not exceed 0.7 mg/l [28].

It was found in [11, 26, 29] that perchlorate forms as a byproduct during the ozonation of chloride solutions. Perchlorate ions are very dangerous during pre-natal development and for the developing infant organism [30].

There is one more serious risk in the use of ozonated physiological salines that is not related to the reaction of ozone with chloride ions. Physiological salines can contain bromide ions (bromides are permanent satellites of natural chlorides), and their quantity is not regulated [31]. Bromide ions are easily oxidized by ozone; in a neutral medium at relatively short ozonation times, the main product of this reaction is hypobromic acid HOBr [32, 33]. Under some conditions, however, bromide can be completely transformed into bromate BrO_3^- [32, 33], a probable carcinogen [34]. The formation of bromate must necessarily be taken into account when the applications of ozonated physiological salines in medical practice are considered.

CONCLUSIONS

The presence of hypochloric acid, chlorate, perchlorate, hypobromic acid, and bromate is possible in ozonated physiological salines. To assess the possibility of using a preparation in medicine, we must employ sensitive methods for the determination of these substances and to establish the conditions under which their concentrations do not exceed acceptable values. This question was not raised in [2, 3]. In our opinion, the results of [2, 3] cannot be considered as substantiation of the safety (i.e., that the concentrations of HOCl , ClO_3^- , ClO_4^- , HOBr , BrO_3^- are acceptable) of ozonated physiological salines.

Reaction (1) of chloride-ion oxidation by ozone via electron transfer thus does not occur due to its extremely high endoergicity and negligibly slow rate. Any of the processes supposedly caused by this reaction (1) (particularly ozone decomposition in sodium chloride solution via scheme (1)–(4)) do not occur either. The assumption that reaction (1) is the primary

stage of ozone interaction with chloride ions contradicts the experimental data on the products and kinetic regularities of the interaction of ozone with chloride ions. In order to estimate the possibility of using an ozonated physiological saline in medicine, the formation of chloride-ion oxidation products and ozonation byproducts must be taken into account.

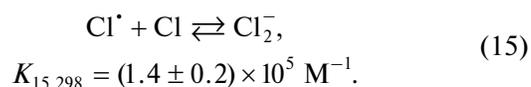
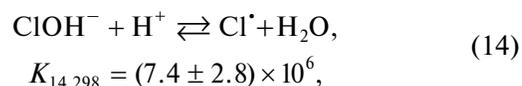
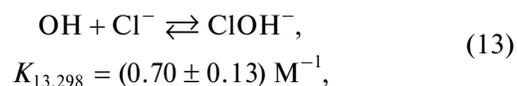
ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 10-05-01136-a.

APPENDIX

Standard Gibbs Energies of Formation for Cl^\cdot , Cl_2^- , and ClOH^- in Aqueous Solution at 25°C

Gibbs energies of formation of Cl^\cdot , Cl_2^- , and ClOH^- can be found in the well-known review [35], devoted to the thermodynamic properties of inorganic free radicals in aqueous solutions. However, the data of [35] are somewhat obsolete. More reliable estimates of the equilibrium constants' values for reactions of chlorine atoms in aqueous solutions have recently appeared in the literature. These new data allow us to obtain more precise values for the thermodynamic properties of Cl^\cdot , Cl_2^- , and ClOH^- . Our calculations were based on the equilibrium constants' values for reactions of chlorine atoms presented in [16]:



The Gibbs energies of the formation of Cl^\cdot , Cl_2^- , and ClOH^- in aqueous solution are linear combinations of Gibbs energies for reactions (13)–(15), water self-ionization reaction



and Gibbs energies of formation of OH radical (25.5 ± 0.6 kJ/mol) [36], Cl^- (−131.228 kJ/mol) [6], and OH^- (−157.224 kJ/mol) [6]:

$$\begin{aligned} \Delta_f G^\circ(\text{Cl}^\cdot) &= \Delta_{13} G^\circ + \Delta_{14} G^\circ + \Delta_{16} G^\circ \\ &+ \Delta_f G^\circ(\text{OH}) + \Delta_f G^\circ(\text{Cl}^-) - \Delta_f G^\circ(\text{OH}^-), \\ \Delta_f G^\circ(\text{Cl}_2^-) &= \Delta_{13} G^\circ + \Delta_{14} G^\circ + \Delta_{15} G^\circ + \Delta_{16} G^\circ \\ &+ \Delta_f G^\circ(\text{OH}) + 2\Delta_f G^\circ(\text{Cl}^-) - \Delta_f G^\circ(\text{OH}^-), \end{aligned}$$

Standard Gibbs energies of formation for Cl^\bullet , Cl_2^- , and ClOH^- in aqueous solution at 25°C, kJ/mol

Compound	This work	Data of [35]
$\text{Cl}^\bullet(\text{aq})$	93.1 ± 1.6	101
$\text{Cl}_2^-(\text{aq})$	-67.5 ± 2.0	-61
$\text{ClOH}^-(\text{aq})$	-104.8 ± 1.1	-104

$$\Delta_r G^\circ(\text{ClOH}^-) = \Delta_{13} G^\circ + \Delta_r G^\circ(\text{OH}) + \Delta_r G^\circ(\text{Cl}^-).$$

The obtained values are presented in the table.

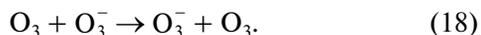
Our estimates of the Gibbs energies of formation of Cl^\bullet , Cl_2^- , and ClOH^- are slightly lower than those presented in [35]. This is evidence that radicals Cl^\bullet , Cl_2^- , and ClOH^- are somewhat more stable in aqueous solutions than was considered earlier.

Estimating the Reorganization Energy for Reaction (1)

It is possible to calculate reorganization energy λ_1 for reaction (1) using the following expression [5]:

$$\lambda_1 = (\lambda_{\text{Cl}/\text{Cl}^-} + \lambda_{\text{O}_3/\text{O}_3^-})/2,$$

where $\lambda_{\text{Cl}/\text{Cl}^-}$ and $\lambda_{\text{O}_3/\text{O}_3^-}$ are reorganization energies caused by self-exchange reactions



In general, reorganization energy λ is the sum of reorganization energies of bonds λ_i (inner sphere) and the solvent λ_o (outer sphere) [4, 5]. For reaction (17), $\lambda_{i,17} = 0$ kJ/mol, $\lambda_{o,17} = 211$ kJ/mol, $\lambda_{\text{Cl}/\text{Cl}^-} = 211$ kJ/mol. The value $\lambda_{o,17}$ is obtained on the basis of the so-called “separate” reorganization energies of the chlorine atom (132.4 kJ/mol) and chloride ion (251.9 kJ/mol) calculated in [37]. For reaction (18), $\lambda_{i,18} = 44$ kJ/mol [38], $\lambda_{o,18} = 200$ kJ/mol [39], wherefrom $\lambda_{\text{O}_3/\text{O}_3^-} = 244$ kJ/mol. The obtained values of reorganization energies for self-exchange reactions (17), (18) allow one to calculate reorganization energy $\lambda_1 = 227.5$ kJ/mol, wherefrom Gibbs energy of activation for reaction (1) $\Delta_1 G^{\ddagger} = 138$ kJ/mol.

From formula (6), we find that the rate constant of reaction (1) $k_1 = 8 \times 10^{-15}$ 1/(mol s) at 25°C. According to (12), the effective rate constant of ozone decomposition in a 0.15 M solution of NaCl $k_{\text{O}_3} = 4 \times 10^{-14}$ s⁻¹, corresponding to a half-life of $\sim 6 \times 10^5$ years.

REFERENCES

1. A. V. Levanov, E. E. Antipenko, and V. V. Lunin, Russ. J. Phys. Chem. A **86**, 519 (2012).
2. S. D. Razumovskii, M. L. Konstantinova, T. V. Grinevich, et al., Kinet. Catal. **51**, 492 (2010).
3. S. D. Razumovskii, G. V. Korovina, and T. V. Grinevich, Dokl. Phys. Chem. **434**, 163 (2010).
4. R. A. Marcus, Rev. Mod. Phys. **65**, 599 (1993).
5. L. Ebersson, *Electron Transfer in Organic Chemistry* (Springer, Berlin, New York, Heidelberg, 1987).
6. D. D. Wagman, W. H. Evans, V. B. Parker, et al., J. Phys. Chem. Ref. Data, No. 11 (Suppl. 2) (1982).
7. W. H. Koppenol, D. M. Stanbury, and P. L. Bounds, Free Rad. Biol. Med. **49**, 317 (2010).
8. *CRC Handbook of Chemistry and Physics*, 84th ed., Ed. by D. R. Lide (CRC Press, Boca Raton, FL, 2003).
9. R. Atkinson, D. L. Baulch, R. A. Cox, et al., Atmos. Chem. Phys. **7**, 981 (2007).
10. G. Gordon and B. Bubnis, Ozone Sci. Eng. **21**, 447 (1999).
11. B. Rao, T. A. Anderson, A. Redder, and W. A. Jackson, Environ. Sci. Technol. **44**, 2961 (2010).
12. K. Suma, Y. Sumiyoshi, Y. Endo, et al., J. Phys. Chem. A **108**, 8096 (2004).
13. S. P. Sander, R. R. Friedl, D. M. Golden, et al., JPL Publication No. 06-2 (Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 2006).
14. M. A. A. Clyne and J. A. Coxon, Proc. R. Soc. London A **303**, 207 (1968).
15. S. C. Wofsy and M. B. McElroy, Can. J. Chem. **52**, 1582 (1974).
16. X. Y. Yu, J. Phys. Chem. Ref. Data **33**, 747 (2004).
17. B. H. J. Bielski, Rad. Phys. Chem. **41**, 527 (1993).
18. W. R. Haag and J. Hoigne, Water Res. **17**, 1397 (1983).
19. J. Hoigne, H. Bader, W. R. Haag, and J. Staehelin, Water Res. **19**, 993 (1985).
20. A. V. Levanov, I. V. Kuskov, A. V. Zosimov, et al., Kinet. Catal. **44**, 740 (2003).
21. V. V. Lunin, A. V. Levanov, I. V. Kuskov, et al., Russ. J. Phys. Chem. A **77**, 580 (2003).
22. J. C. Morris, J. Phys. Chem. **70**, 3798 (1966).
23. E. J. Hart, K. Sehested, and J. Holcman, Anal. Chem. **55**, 46 (1983).
24. M. L. Kilpatrick, C. C. Herrick, and M. Kilpatrick, J. Am. Chem. Soc. **78**, 1784 (1956).
25. G. Grguric, J. H. Trefry, and J. J. Keaffaber, Water Res. **28**, 1087 (1994).
26. N. Kang, W. A. Jackson, P. K. Dasgupta, and T. A. Anderson, Sci. Total Environ. **405**, 301 (2008).
27. A. V. Levanov, I. V. Kuskov, E. E. Antipenko, and V. V. Lunin, Russ. J. Phys. Chem. A **82**, 2045 (2008).
28. *Chlorite and Chlorate in Drinking-Water. Background Document for Development of WHO Guidelines for Drinking-Water Quality*, WHO/SDE/WSH/05.08/86 (World Health Organization, Geneva, 2005).

29. P. K. Dasgupta, P. K. Martinelango, W. A. Jackson, et al., *Environ. Sci. Technol.* **39**, 1569 (2005).
30. A. M. Leung, E. N. Pearce, and L. E. Braverman, *Best Practice Res. Clin. Endocrinol. Metabolism* **24**, 133 (2010).
31. *State Pharmacopoeia of USSR* (Meditsina, Moscow, 1968) [in Russian].
32. W. R. Haag and J. Hoigné, *Environ. Sci. Technol.* **17**, 261 (1983).
33. U. Von Gunten and J. Hoigne, *Environ. Sci. Technol.* **28**, 1234 (1994).
34. *Bromate in Drinking-Water. Background Document for Development of WHO Guidelines for Drinking-Water Quality*, WHO/SDE/WSH/05.08/78 (World Health Organization, Geneva, 2005).
35. D. M. Stanbury, *Adv. Inorg. Chem.* **33**, 69 (1989).
36. H. A. Schwarz and R. W. Dodson, *J. Phys. Chem.* **88**, 3643 (1984).
37. C. Hartnig and M. T. M. Koper, *J. Chem. Phys.* **115**, 8540 (2001).
38. D. M. Stanbury, *Adv. Chem.* **253**, 165 (1997).
39. X. Y. Li, L. L. Zhao, and S. Q. Xiao, *Theor. Chem. Acc.* **105**, 77 (2000).