



The Reaction of Chlorine(III) with Bromine and Hypobromous Acid: Kinetics and Mechanism

Thesis of doctoral disseratation

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1. Introduction and objectives

Due to their chemical properties – variable redox potentials, high reactivity – halogens and oxyhalogens have great importance on several fields, for example in industrial processes, atmospheric chemistry and nonlinear kinetic phenomena. The reactions of these compounds are complex, and typically proceed via reactive intermediates.

The reactions of halogens and oxyhalogens are important in drinking water disinfection and wastewater treatment. Several kinds of disinfectants are used such as free chlorine, chlorine dioxide, chloramines and ozone. Each of them has its advantage and disadvantage in terms of cost, efficacy, stability, ease of application and nature of disinfectant by-products. Some of these by-products are potentially hazardous, for instance the chlorinated aromatic compounds and bromate ion, which are carcinogenic and nephrotoxic. In order to control the formation of these by-products, the mechanism of the aqueous phase reactions of various halogen species need to be known in detail.

Halogens and oxyhalogens also have an important role in the chemistry of the stratosphere. A variety of organic compounds, for example the chlorofluorocarbons (CFCs) and brominated hydrocarbons may generate a number of chlorine and bromine containing free radicals, which participate in ozone destruction cycles. Several oxyhalogen species (ClO , BrO , HOCl , HOBr), which have a central role in this cycle. Much has been learned about the stratospheric chemistry but the details of this cycle, the mechanism of the individual steps is not well understood.

Oxyhalogens are essential components of chemical oscillators. Chemical oscillators with bromate ion as an essential component are known as bromate-driven oscillators. They were among the first to be discovered (i.e. the Belousov-Zhabotinsky reaction). The first systematically designed family of chemical oscillators are based on the reactions of chlorite ion. Because of its relative simplicity, the chlorite ion – iodide ion reaction, the so-called “minimal oscillator”, has been used as a model system for experimental studies of nonlinear phenomena. The chlorite ion is perhaps the most readily available source of nonlinear behavior in chemistry. In most of its reactions, whether it is acting as an oxidizing or a reducing agent, it triggers some sort of unconventional kinetics. Several models were created to simulate the complex behavior of oscillating systems, but many steps, for instance the reaction of chlorite ion with bromine species are not described in full detail.

The aim of this work was to develop a kinetic model on the basis of a new set experimental data for the $\text{Br}_2/\text{HOBr} - \text{HClO}_2/\text{ClO}_2^-$ reaction system, thus to provide a theoretical background for the practical applications.

2. Applied methods and equipments

Bromine stock solutions were prepared by distilling Br_2 into $\sim 0.1 \text{ M}$ HClO_4 solution. They were stored in and dispensed from a home-built, electronic “shrinking bottle”. With this device bromine solutions could be stored with less than 1% concentration loss per day.

Bromide-free hypobromous acid solutions were prepared in the reaction of equimolar amounts of alkaline bromine solution and silver perchlorate. Disproportionation of HOBr in the freshly prepared stock solution was negligible for several hours. However, a significant decrease in the HOBr concentration occurred within a day thus the solutions were prepared freshly every day.

The ionic strength was adjusted to 1.0 M with NaClO_4 . The reagent solutions were prepared in doubly deionized and ultra-filtered water obtained from a Milli-Q RG (Millipore) water purification system.

The pH-metric and iodometric titrations were carried out by using a *Metrohm* 6.0202.000 combined glass electrode and a *Metrohm* 6.0420.100 combined Pt-electrode connected to a *Metrohm* 721 *NET Titrino* titrator controlled by the *TiNet* 2.1 program.

Spectrophotometric measurements were performed with an HP-8453 and a Shimadzu UV-3101 spectrophotometer. Fast kinetic measurements were made with an Applied Photophysics DX-17 MV sequential stopped-flow instrument using either in the single-wavelength detection mode or with an Applied Photophysics PDA 1 diode array detector. Laser flash photolytic experiments were performed with an Applied Photophysics instrument. The irradiation wavelength, 355 nm, was provided by the third harmonic of a Nd :YAG laser. At longer reaction times, time-resolved spectra were recorded on the HP-8453 spectrophotometer equipped with an RX2000 Rapid Kinetic Spectrometer Accessory (Applied Photophysics). All measurements were made at $25 \pm 0.1 \text{ }^\circ\text{C}$.

The number of data points in the experimental kinetic curves was 400-800, but was reduced to approximately 100 points with a spline smoothing algorithm. The time scale was corrected for $t = 0$ and all the calculations were carried out with these modified curves. During calculations the chemical model was represented with an ordinary differential equation system (ODE). All reaction steps were considered to be elementary. The ODE was integrated with the *ZITA 4.0* program package, based on the Gear-algorithm. First the concentration – time profiles were calculated for every species under different experimental conditions, and from these profiles the absorbance – time curves were derived by using the molar absorptivities. Comparing these calculated curves with the experimental traces, the characteristic relative standard deviation for the model could be determined.

3. Results

We studied the mechanism of the $\text{Br}_2/\text{HOBr} - \text{HClO}_2/\text{ClO}_2^-$ reaction system, in which the following oxidizing agents of chlorine(III) were identified: Br_2 ; Br_2^- , the product of the oxidation by bro-

mine; HOBr formed in the bromine hydrolysis process; and Br radical, produced by the dissociation of the dibromine radical anion. In a complex system like this, experimental limitations and cross-correlation between the parameters may introduce some uncertainty in the fitting procedure whenever all relevant constants are estimated simultaneously. Thus, the test of the model would require that the kinetic features of all individual steps are known independently.

1. The formation constant of tribromide ion was determined by generating Br_2 in the reaction of bromate ion with excess bromide ion: $K = 19.3 \pm 1.2 \text{ M}^{-1}$.
2. The hydrolysis constant of bromine was determined spectrophotometrically. To avoid its evaporation, bromine was prepared by mixing NaBr and HOBr solutions in a sealed cell. The spectra were evaluated using a nonlinear least-squares fitting routine. The equilibrium constant is $(7.17 \pm 0.04) \times 10^{-9} \text{ M}^2$.
3. There are two kinetically well-separated phases in the $\text{Br}_2 - \text{ClO}_2^-$ reaction. In the first phase the fast absorbance change was consistent with the consumption of bromine and the formation of chlorine dioxide. At longer reaction times, the absorbance slightly increases both in the UV and in the visible region, probably due to the formation of tribromide ion and chlorine dioxide, which are formed in the subsequent reaction of chlorite ion with bromide ion. The $\text{Br}^- - \text{ClO}_2^-$ reaction is relatively slow and kinetically coupled with the acid-catalyzed decomposition of chlorite ion, which also produces chlorine dioxide. Because of these coupled reactions a uniform final stoichiometry cannot be given for the overall process. However, in the first phase the spectral changes were consistent with the following stoichiometry: $\text{Br}_2 + 2\text{ClO}_2^- = 2\text{Br}^- + 2\text{ClO}_2$.
4. Since in most cases the stopped-flow traces could not be fitted with a single-exponential function, the reaction orders for reactant were estimated by using the initial-rate method. The initial phase of the reaction was roughly first order with respect to both chlorite ion and bromine.
5. It was shown that the oxidation with bromine predominantly occurs with the ClO_2^- form of Cl(III), and in the presence of excess Br^- and at $\text{pH} < 3$, the variation of the reaction rate as a function of pH can be understood in terms of the acid dissociation equilibrium of chlorous acid.
6. Both bromide ion and chlorine dioxide has a pronounced retarding effect on the reaction rate.
7. Time-resolved spectra are consistent with steady formation of chlorine dioxide, and the small absorbance values extrapolated to $t = 0$ can be interpreted by taking into account the absorbing species in the reagent solutions. The experimental data do not confirm the formation of any new absorbing species. However these findings do not exclude the possibility that BrClO_2 is formed at low concentration levels and plays an important kinetic role in this system.
8. In the first step of the oxidation of chlorine(III) by bromine, dibromine radical anion is formed. This step is not favored thermodynamically. The rate constant of the backward reaction, the $\text{Br}_2^- - \text{ClO}_2$ process, was determined by laser flash photolysis under pseudo first order conditions. The

reaction was kinetically coupled with the second order self-decay process of dibromine radical anion. Accordingly, the kinetic curves were fitted to a mixed first and second order equation. The rate constant is $(3.56 \pm 0.06) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, which is independent of ionic strength and pH.

9. To understand the kinetic role of HOBr in the $\text{Br}_2 - \text{ClO}_2^-$ reaction system, we studied the HOBr – Cl(III) reaction independently under the same conditions. Kinetic traces obtained with excess ClO_2^- consist of two well-separated stages. The first section corresponds to the fast reaction of chlorine(III) with HOBr producing ClO_2 and Br^- , and the slower one to the reaction of chlorite ion with bromine formed in the first stage. Reactions with excess HOBr was not biphasic. Because of the complexity of the kinetics the reaction orders for the reactants were estimated by using the initial-rate method. The kinetic traces were fitted to a polynomial function. The order of the reaction is one with respect to HOBr but is between 1 and 2 with respect to Cl(III).
10. Under the conditions applied ($\text{pH} = 1.50$) the major form is HClO_2 . We proposed the formation of BrClO_2 directly in the reaction of HClO_2 and HOBr, and the formation of ClO_2 and Br^- in a subsequent reaction of BrClO_2 and ClO_2^- . Experimental initial rates (v_0) measured at constant pH and at constant HOBr and Cl(III) concentrations were fitted by equations derived on the basis of the proposed rate expression. The goodness of the fit and the consistency of the protonation equilibrium constant of chlorous acid with the literature values support the validity of the rate expression and mechanism proposed.
11. A detailed mechanism was proposed for the interpretation of the HOBr – Cl(III) reaction, which besides the actual redox steps, contains the bromine hydrolysis, the equilibrium of the formation of tribromide and the deprotonation of the chlorous acid as fast preequilibria. The kinetic model was represented by an ordinary differential equation system, which was solved with the Gear algorithm. The agreement between the measured and calculated traces confirms the validity of the proposed mechanism.
12. A ten-step kinetic model was proposed for the interpretation of the $\text{Br}_2/\text{HOBr} - \text{HClO}_2/\text{ClO}_2^-$ reaction system. Some of the rate constants of the individual steps were determined independently (see above), some of them were known from the literature or were assumed to be diffusion controlled. The rate constants of the remaining steps were calculated by fitting the experimental curves measured under different conditions by the postulated kinetic model. To test the validity of the proposed model we compared the experimental and calculated kinetic curves and we found reasonably good agreement between the corresponding traces.
13. This model provides a coherent interpretation of the bromide ion and chlorine dioxide dependence of the reaction rate. In the absence of bromide ion bromine radical and hypobromous acid react with chlorite ion in fast reactions. When the concentration of bromide ion is increased, the recombination of Br_2^- becomes faster and the bromine hydrolysis is suppressed, the concentrations of the bromine radical and the hypobromous acid decrease. Consequently, the contribution of the Br –

ClO_2^- and $\text{HOBr} - \text{ClO}_2^-$ reactions to the oxidation process becomes negligible by increasing the bromide ion concentration. The model explains the retarding effect of chlorine dioxide on the reaction rate by its reaction with dibromine radical anion. This reaction suppresses the first, thermodynamically unfavoured oxidation step. The role of the bromide ion in this retarding effect is that it increases the kinetic weight of the inhibition step by suppressing the competing reaction paths.

Table 1. The kinetic model of the $\text{Br}_2 - \text{ClO}_2^-$ reaction

reaction	no.	log K	rate. const.	rate const. values ^a
$\text{Br}_2 + \text{ClO}_2^- = \text{Br}_2^- + \text{ClO}_2$	R1	-5.93	k_1	$(4.84 \pm 0.02) \times 10^3$
			k_{-1}	3.56×10^9
$\text{Br}_2^- + \text{ClO}_2^- = \text{ClO}_2 + 2\text{Br}^-$	R2	11.40	k_2	$(3.10 \pm 0.08) \times 10^6$
			k_{-2}	1.2×10^{-5}
$\text{Br}_2 + \text{Br}^- = \text{Br}_3^-$	R3	1.28	k_{-3}	1.5×10^9
			k_3	7.8×10^7
$\text{ClO}_2^- + \text{H}^+ = \text{HClO}_2$	R4	1.72	k_4	1.0×10^{10}
			k_{-4}	1.9×10^8
$\text{Br}_2 = \text{HOBr} + \text{Br}^- + \text{H}^+$	R5	-8.14	k_5	1.1×10^2
			k_{-5}	1.5×10^{10}
$\text{Br} + \text{Br}^- = \text{Br}_2^-$	R6	5.04	k_6	1.0×10^{10}
			k_{-6}	9.1×10^4
$\text{Br} + \text{Br} = \text{Br}_2$	R7	27.35	k_7	1.0×10^{10}
			k_{-7}	4.5×10^{-18}
$\text{Br} + \text{ClO}_2^- = \text{Br}^- + \text{ClO}_2$	R8	16.37	k_8	$(3.9 \pm 0.4) \times 10^9$
			k_{-8}	1.7×10^{-7}
$\text{HOBr} + \text{HClO}_2 = \text{BrClO}_2 + \text{H}_2\text{O}$	R9		k_9	$(3.34 \pm 0.02) \times 10^4$
			k_{-9}	$(3.5 \pm 1.3) \times 10^3$
$\text{BrClO}_2 + \text{ClO}_2^- = 2\text{ClO}_2 + \text{Br}^-$	R10		k_{10}	$(2.9 \pm 1.0) \times 10^7$

^a The units for the first-, second-, and third-order rate constants are s^{-1} , $\text{M}^{-1}\text{s}^{-1}$ és $\text{M}^{-2}\text{s}^{-2}$.

4. The results and some of their possible applications

The results presented here confirm that in the $\text{Br}_2/\text{HOBr} - \text{HClO}_2/\text{ClO}_2^-$ reaction system the oxidation of the chlorite ion occurs in competing parallel redox steps, under acidic conditions. The concentration ratios of the oxidants, Br_2^- , Br and HOBr , as well as the relative rates of the parallel reactions, are controlled by the bromide ion concentration and the pH. The proposed model may lead to a better understanding of the mechanistic details of complex reactive systems that contain bromine and chlorite ion. The results may prove to be significant in studying the formation of by-products in water disinfection. Furthermore, the same results can help to clarify the role of halogens and oxyhalogens in stratospheric chemistry and oscillation reactions.

5. Publications

Publications on the field of the dissertation:

1. Zs. Tóth, I. Fábián
Kinetics and Mechanism of the Initial Phase of the Bromine – Chlorite Ion Reaction in Aqueous Solution
Inorganic Chemistry **2000**, 39, 4608-4614.
2. Zs. Tóth, I. Fábián, A. Bakac
A Flash Photolytic Study of the Reaction Between Chlorine Dioxide and Dihalogen Radical Anions
Inorganic Reaction Mechanisms **2001**, 3, 147-152.
3. Zs. Tóth, I. Fábián
Kinetics and Mechanism of Hypobromous Acid – Chlorite Ion Reaction in Aqueous Solution
Inorganic Chemistry, to be submitted

Lectures and posters on the field of the dissertation:

1. Tóth Zs., Fábián I.
Reactions of bromine with oxyhalogen compounds: $\text{Br}_2 - \text{ClO}_2^-$
XXXIII. Symposium of Coordination Chemistry, 1998, Paks
(lecture)
2. Zs. Tóth, I. Fábián
Mechanistic Aspects of the Bromine - Chlorite Ion Reaction in Aqueous Solution
Fast Reactions in Solutions Discussion Group, 1998, Bielefeld, Németország
(lecture)
3. Zs. Tóth, I. Fábián
The Oxidation of Chlorite Ion by Bromine and Hypobromous Acid. The Early Phase.
Inorganic Mechanism Discussion Group Meeting'98, 1999, Cambridge, UK
(lecture)
4. Tóth Zs., Fábián I.
Reactive Intermediates in the Redox Reactions of Simple Inorganic Compounds
XXXIV. Symposium of Coordination Chemistry, 1999, Tata
(lecture)
5. Tóth Zs. (témavezető: Dr. István Fábián)
Reactions of Bromine with Oxyhalogen Compounds: $\text{Br}_2 - \text{ClO}_2^-$
National Students Scientific Circle Conference, 1999, Veszprém
(lecture)

6. Zs. Tóth, I. Fábián, A. Bakac

Oxidation Kinetics of Dibromine Radical Anion by Chlorine Dioxide

Inorganic Reaction Mechanisms: Insights into Chemical Challenges, 2002, Kloster Banz, Germany
(poster)

7. Zs. Tóth, I. Fábián, A. Bakac

Reactions of Intermediates in the Bromine – Chlorite Ion Reaction System

Kinetic Workshop, 2002, Balatonalmádi
(lecture)