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Rate constants for the reactions of free radicals, including  $e_{aq}^{-}$ , 'OH, SO<sub>4</sub><sup>--</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sub>2</sub><sup>--</sup> (Cl'), with oxychloride compounds have been determined. The free radicals were generated by pulse radiolysis and laser photolysis. Most of the reactions have nearly diffusion-controlled rate constants (>10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>). ClO<sup>-</sup> has relatively higher reactivity than its acid form.  $e_{aq}^{-}$  reacts with oxychloride compounds to form their electron adducts which dissociate easily. Electron transfer reactions occur between 'OH, SO<sub>4</sub><sup>--</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sub>2</sub><sup>--</sup> (Cl') radicals and the oxychloride ions. The kinetics results obtained here can be used in simulation work to understand the radiation-induced reactions taking place in groundwater which are relevant to the geological aspects of radioactive waste storage and disposal.

## 1 Introduction

Free radicals participate as important intermediates in the chemical changes that occur in the atmosphere. Since the early 1970s, it has become increasingly evident that man's release of chlorofluorocarbons and other halogen-containing compounds has an impact on stratospheric ozone. The monoxides of the halogens, XO' (ClO', BrO', IO' and possibly FO') are central to the chemistry that occurs. Participation of XO' radicals and related species in tropospheric chemistry has also become recognized. Recently, the chemistry of halogen oxides in the troposphere has been reviewed by Wayne et  $al.^1$  In addition, since the review of Graedel and Weschler,<sup>2</sup> modelling studies have shown that reactions of free radicals, including OH, SO<sub>4</sub><sup>--</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sub>2</sub><sup>--</sup> (Cl<sup>-</sup>) and CO<sub>3</sub><sup>--</sup> in cloud water may play important roles in the atmospheric oxidation of SO<sub>2</sub> to sulfuric acid. Atmospheric aqueous phase chemistry, which comprises a wide variety of inorganic and organic radical reactions, also has impact on the gas-phase budget of stable oxidants such as H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> and on radicals such as 'OH,  $HO_2$  and  $NO_x$ .<sup>3-6</sup>

Additionally, these inorganic radicals have also been suggested to be of potential importance in the chemistry of irradiated groundwater, relevant to the storage of radioactive waste.<sup>7</sup> Chloride ion is assumed to be one of the predominant solutes dissolved in groundwater, especially sea water. Recently, in our unpublished work,  $\text{ClO}_3^-$  was detected as one of the final products from the  $\gamma$ -radiolysis of Cl<sup>-</sup> solution. It can be suggested that  $\text{ClO}_x^-$  ions and  $\text{ClO}_x^-$  radicals are involved in the oxidation processes from Cl<sup>-</sup> to  $\text{ClO}_3^-$ . Thus studies of the kinetics and the stable products formed in the radiolysis of chloride ion and oxychloride compounds and their redox reactions with radiation-induced primary radicals, such as 'OH,  $e_{eq}^-$  and H', and the secondary inorganic free radicals in aqueous solutions, will help us to understand the radiation-induced reactions taking place in groundwater.

Pulse radiolysis and its complementary tool, laser photolysis can be used for kinetics studies on reactions of free radicals. There have been some reports of the rate constants of the reaction of  $e_{aq}^{-}$  and 'OH with ClO<sup>-</sup> and ClO<sub>2</sub><sup>-</sup>,<sup>8-11</sup> and 'OH with ClO<sub>2</sub><sup>.12,13</sup> Although the rate constants for the reactions of 'OH, SO<sub>4</sub><sup>--</sup> and NO<sub>3</sub>' with Cl<sup>-</sup> have also been

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studied in detail,<sup>14</sup> there is little information on the rate constants for the reactions of  $SO_4^{--}$ ,  $NO_3^{-}$  and  $Cl_2^{--}$  (Cl<sup>-</sup>) with the oxychlorides. In our previous paper,<sup>15</sup> the electron transfer reactions of  $SO_4^{--}$  and  $NO_3^{--}$  with  $ClO_3^{--}$  to yield  $ClO_3^{--}$ radicals were studied by laser photolysis. Here, the rate constants for the reactions of  $e_{aq}^{--}$ , 'OH,  $SO_4^{--}$ ,  $NO_3^{-}$ , and  $Cl_2^{--}$ (Cl<sup>-</sup>) with chloride ion and oxychloride compounds in aqueous solutions have been determined systematically by pulse radiolysis and laser photolysis. Various methods for the generation of free radicals were utilized, including the direct radiation of concentrated solutions to produce  $SO_4^{--}$ ,  $NO_3^{-}$  and  $Cl_2^{--}$  radicals that has been studied previously.<sup>16-21</sup> Some results were compared with the literature data.

## 2 Experimental

### 2.1 Pulse radiolysis and laser photolysis

Pulse radiolysis experiments were performed by using an electron pulse of 10 ns and 28 MeV from a linear accelerator at the Nuclear Engineering Research Laboratory, the University of Tokyo. Details have been given elsewhere.<sup>22</sup> The absorbed dosage was determined to be *ca*. 10 krad per pulse by using  $10^{-2}$  mol dm<sup>-3</sup> KSCN solution saturated with N<sub>2</sub>O and a *G*  $a(SCN)_2^-$  of 51 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> (100 eV)<sup>-1</sup> at 475 nm.<sup>23</sup> Laser photolysis experiments were performed with an excimer laser (LAMBDA PHYSIK LEXTRA 100) which provides 351 nm (XeF) or 248 nm (KrF) light with energy of 50 or 330 mJ per pulse, respectively, for a duration of 20 ns. This system has been described in detail, previously.<sup>15</sup>

#### 2.2 Chemicals

Aqueous solutions of chlorine dioxide (ClO<sub>2</sub><sup>-</sup>) were prepared as follows:<sup>24</sup> ClO<sub>2</sub><sup>-</sup> was prepared by reacting 0.1 mol dm<sup>-3</sup> peroxosulfate with *ca*. 0.02–0.05 mol dm<sup>-3</sup> of chlorite for 4 h at 60 °C. The ClO<sub>2</sub><sup>-</sup> formed within hours, and was transferred with a stream of argon into a washing bottle containing icecooled distilled water and then collected in water in an amber bottle. The reaction was conducted away from all direct light and behind an explosion shield. The ClO<sub>2</sub><sup>-</sup> solution was stored in the dark in a refrigerator. For reactions of ClO<sub>2</sub><sup>-</sup> with hydroxyl radical or hydrated electron, it was transferred

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from the deaerated stock solution into deaerated water in a 1 cm cell, by bubbling with N<sub>2</sub>O or argon gas, respectively. Before irradiation, the concentration of ClO<sub>2</sub> was determined spectrophotometrically by using an  $\varepsilon$ -value at 358 nm of 1250 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.<sup>24</sup>

Sodium hypochlorite solution was prepared by the method of Taylor and Bostock<sup>25</sup> by distilling a mixture of 35 g of boric acid and 12 g of Ca(ClO)<sub>2</sub> in 600 ml of water. The first 100 ml of distillate was collected in 200 ml containing 1 g NaOH to give *ca*. 0.04 mol dm<sup>-3</sup> ClO<sup>-</sup> solution at pH *ca*. 12. Three methods were used to determine the concentration of ClO<sup>-</sup> accurately. The first was the measurement of I<sub>3</sub><sup>-</sup> from reaction of KI with ClO<sup>-</sup> in the buffered solution of C<sub>6</sub>H<sub>4</sub>COO<sup>-</sup>(H<sup>+</sup>), by spectrophotometer at 351 nm taking  $\varepsilon = 26400$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at pH 5. The second was the titration of I<sub>3</sub><sup>-</sup> with S<sub>2</sub>O<sub>3</sub><sup>-</sup> after the reaction of ClO<sup>-</sup> with KI had been completed and the third was the measurement of ClO<sup>-</sup> by spectrophotometry at 292 nm taking  $\varepsilon = 360$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. The results from the three methods agreed very well.

Other chemicals were guaranteed reagents, solutions were prepared with Millipore water and the measurements were carried out at room temperature (*ca.*  $20 \,^{\circ}$ C).

#### 2.3 Kinetic analyses

Ideal conditions were chosen such that only one primary radical was present and the concentration of the reactive solute was high enough to ensure that pseudo-first-order kinetics were applicable. The absolute rate constants were obtained by direct observation of the decay of the transient or the growth of its product, whichever had a suitable absorption spectrum. When neither the primary radical nor the reaction product could be observed directly, the relative rate constants were deduced from measurements of product yields using the competition method. A simulation method was used for kinetic analysis of the complex reactions and the overlapping absorbances of the transient species with the program FAC-SIMILE (AEA Technology, Harwell).

If both reactants were charged, the rate constants were corrected for the primary kinetic salt effect by using the Brønsted–Bjerrum equation:

$$\log(k/k_0) = 1.02Z_a Z_b I^{1/2} (1 + I^{1/2})^{-1}$$
(I)

where k and  $k_0$  are the rate constants at ionic strength I and zero,  $Z_a$  and  $Z_b$  are the charges of reactants, respectively. Note that, in the case of high ionic strength I, the corrected values obtained by this equation were just rough estimations.

#### **3** Results and Discussion

#### 3.1 Reactions with $e_{aq}^{-}$

For reactions of oxychlorides with  $e_{aq}^{-}$ , solutions were bubbled with argon before irradiation. Since the  $pK_a$  value of HClO is 7.52,<sup>26</sup> the pH values of HClO solutions for irradiation were adjusted to 5 with appropriate amounts of HClO<sub>4</sub> in which 99% of ClO<sup>-</sup> existed in its acid form. For reactions of other oxychlorides, the pH values of the solutions were adjusted above 10 with NaOH in order to avoid  $e_{aq}^{-}$  decaying rapidly with other substrates such as H<sup>+</sup>. The rate constants were determined from the decay kinetics of  $e_{aq}^{-}$  at 575, 600 or 700 nm. For example, Fig. 1 shows the decay of  $e_{aq}^{-}$ observed at 575 nm from the radiolysis of solutions of different concentrations of ClO<sub>2</sub><sup>-</sup>.

As expected from its standard reduction potential of -2.9 V (as shown in Table 1),<sup>27,28</sup>  $e_{aq}^{-}$  reacts rapidly with many species having more positive reduction potentials. Reactions of oxychlorides with  $e_{aq}^{-}$  and the rate constants, including the



Fig. 1 Transient absorbance, observed at 575 nm, in the pulse radiolysis of aqueous solutions of (a) 0, (b)  $0.48 \times 10^{-4}$ , (c)  $1.5 \times 10^{-4}$ , (d)  $2.9 \times 10^{-4}$  and (e)  $5.6 \times 10^{-4}$  mol dm<sup>-3</sup> ClO<sub>2</sub>, and  $10^{-4}$  mol dm<sup>-3</sup> of NaOH (pH 10), saturated with argon gas. Insert: pseudo-first-order decay rate constants of  $e_{aq}^{-}$  at 575 nm vs. concentrations of ClO<sub>2</sub>.

literature data, are listed in Table 2. Although there has been no previous report of the rate constant for the reaction of  $ClO_2^{\cdot}$  with  $e_{aq}^{-}$ ,  $ClO_2^{\cdot}$  can be suggested to react with  $e_{aq}^{-}$ rapidly because of its high reduction potential of 0.935 V vs. NHE.<sup>12,29,30</sup> Here, the rate constant for reactions of  $ClO_2^{\cdot}$ with  $e_{aq}^{-}$  was determined to be  $(2.1 \pm 0.1) \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.

 Table 1
 Reduction potentials of inorganic couples (mV vs. NHE)

compound or couple X	$E(X/X^{-})$	pH	ref.
aq/e <sub>ag</sub> <sup>-</sup>	-2900		27
-1			28
'OH/OH	1700	neutral	37
	1890	neutral	38
	2700	acid	12
$SO_4^{-}/SO_4^{2-}$	2430		50
NO <sub>3</sub> /NO <sub>3</sub> <sup>-</sup>	2450		51
Cl'/Cl <sup>-</sup>	2410		38
$Cl_{2}^{-}/2Cl^{-}$	2090		38
2 ,	2200	1	52
ClO'/ClO-	1500-1800		53
$ClO_2^{\prime}/ClO_2^{-}$	934	4-6	29
2, 2	936	4-6	30
	934		12
$ClO_2$ , H <sup>+</sup> /HClO <sub>2</sub>	1277	0	54
ClO <sub>3</sub> /ClO <sub>3</sub>	2350		15

Table 2 Rate constants for reactions of oxychlorides with  $e_{aq}^{-}~(10^9\,dm^3\,mol^{-1}\,s^{-1})$ 

reaction	pН	rate constant	comments	ref.
$Cl^- + e_{aa}^- \rightarrow products$		< 10 <sup>-3</sup>		31
$HClO + e_{aa}^{-} \rightarrow Cl^{-} + OH$	5	$0.65 \pm 0.04$		this work
$ClO^- + e_{as}^{aq} \rightarrow Cl^- + O^-$	12.7	$11 \pm 1$	I = 0.05	this work
<b>u</b> .,		$7.5 \pm 0.1$	$I \rightarrow 0$ , from k at $I = 0.05$	
	11	$8.3 \pm 0.4$	I = 0.001	this work
		$7.7 \pm 0.4$	$I \rightarrow 0$ , from k at $I = 0.001$	
	11	7	$I \rightarrow 0$	8
		53		9
		7	$I \rightarrow 0$	10
$ClO_2 + e_{aa} \rightarrow products$	10	$21 \pm 1$		this work
$ClO_2^{-} + e_{ad}^{-} \rightarrow ClO^{-} + O^{-}$	11	$4.4 \pm 0.3$	I = 0.002	this work
1		$4.0 \pm 0.3$	$I \rightarrow 0$ , from k	
			at $I = 0.002$	
		2.5		11
		45		9
$\text{ClO}_3^- + e_{aq}^-$		< 10 <sup>-3</sup>		9



Fig. 2 Decay of ClO<sub>2</sub> observed at 400 nm after the pulse radiolysis of solutions of (a)  $3.8 \times 10^{-4}$  and (b)  $5.6 \times 10^{-4}$  mol dm<sup>-3</sup> ClO<sub>2</sub>, saturated with N<sub>2</sub>O gas. The solid lines are the FACSIMILE curves.

ClO<sup>-</sup> reacts with  $e_{aq}^{-}$  to form Cl<sup>-</sup> and O<sup>-</sup>.<sup>9</sup> Although the rate constant was determined to be  $5.3 \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> in 1972 by Buxton and Subhani,<sup>9</sup> another datum of  $7.3 \times 10^{9}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> was reported by the authors.<sup>10</sup> Before the work of Buxton *et al.*, Anbar and Hart had reported a rate constant of  $7.0 \times 10^{9}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.<sup>8</sup> Here, we determined the rate constant to be  $(1.1 \pm 0.1) \times 10^{10}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 0.05, or  $(8.3 \pm 0.4) \times 10^{9}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 0.001. The corrected rate constants for  $I \rightarrow 0$  were consistent with



Fig. 3 Transient absorption spectra of ClO<sub>2</sub><sup>•</sup> produced from the laser photolysis of solutions of  $1 \times 10^{-2}$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> and  $5 \times 10^{-4}$  mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> at 2 µs after the pulse. Insert: build-up of ClO<sub>2</sub><sup>•</sup>, observed at 358 nm.



**Fig. 4** Transient absorbance, observed at 600 nm, from the pulse radiolysis of solutions of  $5 \times 10^{-3}$  mol dm<sup>-3</sup> NaHCO<sub>3</sub>,  $5 \times 10^{-3}$  mol dm<sup>-3</sup> Na<sub>2</sub>CO<sub>3</sub> and (a) 0, (b)  $1 \times 10^{-3}$ , (c)  $2 \times 10^{-3}$  and (d)  $4 \times 10^{-3}$  mol dm<sup>-3</sup> of NaClO, saturated with N<sub>2</sub>O

those determined by Buxton in 1987<sup>10</sup> and Anbar and Hart in 1968.<sup>8</sup>

There is no literature data for the reaction of HClO with  $e_{aq}^{-}$ . In this work, the reaction was attempted at pH 5. Since the decay of  $e_{aq}^{-}$  increased as the concentration of HClO increased, HClO was observed to react with  $e_{aq}^{-}$ . The product of the reaction was suggested to be Cl<sup>-</sup> and 'OH radical, according to the reaction of ClO<sup>-</sup> with  $e_{aq}^{-}$ . However, the rate constant is one order less than that for the reaction of ClO<sup>-</sup> with  $e_{aq}^{-}$ .

CIO<sup>-</sup> with  $e_{aq}^{-}$ . Reaction of CIO<sub>2</sub><sup>-</sup> with  $e_{aq}^{-}$  to form CIO<sup>-</sup> and O<sup>-</sup> has been studied previously<sup>9,11</sup>. Here, the rate was determined to be  $(4.0 \pm 0.3) \times 10^{9}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at  $I \rightarrow 0$ , which is consistent with that determined by Erikson *et al.*<sup>11</sup> but one order of magnitude less than that determined by Buxton and Subhani.<sup>9</sup> The results reported here and by Erikson seem to be more accurate than that reported earlier.

Reactions of  $Cl^-$ ,  $ClO_3^-$ ,  $ClO_4^-$  with  $e_{aq}^-$  were too slow  $(<10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$  to observe by pulse radiolysis.<sup>9,31</sup>

In general, the mode of reaction of oxychlorides with  $e_{aq}^{-}$  can be represented as the formation of an electron adduct followed by its dissociation:

$$e_{aq}^{-} + \operatorname{ClO}_{x}^{n} \to \operatorname{ClO}_{x}^{n-1} \to \operatorname{ClO}_{x-1}^{n} + \operatorname{O}^{-}$$
(I)

where *n* is the charge on the ion. Thus, reaction of ClO<sub>2</sub><sup>•</sup> with  $e_{aq}^{-}$  can be suggested to form the hypochlorite radical (ClO<sup>•</sup>) and O<sup>-</sup>. The ClO<sup>•</sup> radical then reacts with another ClO<sup>•</sup> in water to form ClO<sub>2</sub><sup>-</sup> and ClO<sup>-</sup>. This will be confirmed by identification of the final products resulting from the  $\gamma$ -radiolysis of ClO<sub>2</sub><sup>•</sup> solution, in future work.

### 3.2 Reactions with 'OH radical

Since the 'OH radical has an absorption band below 300 nm, reactions of the radical are usually observed from another reactant or from the products. Reaction of 'OH with ClO<sub>2</sub>' has been observed from the decay kinetics of ClO<sub>2</sub>' in its irradiated solution of appropriate concentration.<sup>12</sup> Fig. 2 shows the fading decay of ClO<sub>2</sub>' at 400 nm after the radiolysis of N<sub>2</sub>O-saturated solutions of 3.8 and  $5.5 \times 10^{-4}$  mol dm<sup>-3</sup> of ClO<sub>2</sub>'. The rate constant determined here,  $(3.5 \pm 0.5) \times 10^{9}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, was consistent with the value of  $4.0 \times 10^{9}$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> determined by Kläning and Sehested.<sup>12</sup>

ClO<sub>2</sub><sup>•</sup> was also observed as the product from reaction of ClO<sub>2</sub><sup>-</sup> with <sup>•</sup>OH by pulse radiolysis.<sup>11</sup> Here the <sup>•</sup>OH radical was produced by the KrF laser photolysis of H<sub>2</sub>O<sub>2</sub> solution, because of the high quantum yield ( $\Phi = 1$  for  $\lambda > 295$  nm and 1.8 for  $\lambda \approx 250$  nm),<sup>32–34</sup> and the slow reaction of H<sub>2</sub>O<sub>2</sub> with ClO<sub>2</sub><sup>-</sup> (less than 1% of ClO<sub>2</sub><sup>-</sup> was destroyed after 2 h<sup>9</sup>) that can be ignored. About  $2 \times 10^{-5}$  mol dm<sup>-3</sup> of <sup>•</sup>OH was produced from the photolysis of a solution of  $1 \times 10^{-2}$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>. Fig. 3 shows the absorption spectra of ClO<sub>2</sub><sup>-</sup> produced from the photolysis of solutions of H<sub>2</sub>O<sub>2</sub> in the presence of  $5 \times 10^{-4}$  mol dm<sup>-3</sup> of ClO<sub>2</sub><sup>-</sup>. The ClO<sub>2</sub><sup>-</sup> formed was very stable and could be observed over a few ms, during the flash time of the shutter. From the build-up kinetics of ClO<sub>2</sub><sup>-</sup> at 358 nm the rate constant was determined to be (7.9 ± 0.4) × 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which is consistent with that determined by Erikson *et al.*<sup>11</sup> and Buxton and Subhani.<sup>9</sup>

Since  $H_2O_2$  reacts with  $ClO^{-,9,35}$  pulse radiolysis was used to produce 'OH radical for its reaction with  $ClO^{-}$  and HClO. These reactions led to the formation of ClO' radical which has a weak absorption band below 300 nm.<sup>9</sup> Thus the rate constant of  $ClO^{-}$  with 'OH was determined by the carbonate competition method.<sup>9</sup> The sample solutions for irradiation included  $5 \times 10^{-3}$  mol dm<sup>-3</sup> NaHCO<sub>3</sub>,  $5 \times 10^{-3}$  mol dm<sup>-3</sup> Na<sub>2</sub>CO<sub>3</sub> and different concentrations of NaClO under N<sub>2</sub>Osaturation conditions. The pK values of  $H_2CO_3$  and  $HCO_3^{-}$ are 6.4 and 10.3, respectively; the pH value of the solution was *ca*. 10.26 and CO<sub>3</sub><sup>2-</sup> and  $HCO_3^{-}$  existed in the ratio 48 : 52.

Table 3 Rate constants for reactions of oxychlorides with 'OH radical  $(10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ 

reaction	pH	rate constant	comments	ref.
$Cl^- + OH \rightarrow ClOH^-$	2	4.3	decay at 240 nm and build-up at 340 nm, PR	41
		3.0	build-up at 340 nm, PR	42
$HClO + OH \rightarrow ClO + H_2O$	0	$0.14 \pm 0.01$	related to $k(OH + HSO_4)$ , PR	this work
-	<0	$0.11 \pm 0.02$	related to $k(OH + HNO_3)$ , PR	this work
$ClO^- + OH \rightarrow ClO' + OH^-$	10.3	$2.7 \pm 0.1$	related to $k(OH + CO_3^{2^{-}})$ , PR	this work
	11	8.8	related to $k(OH + CO_3^{2})$ , PR	9
$ClO_2 + OH \rightarrow HClO + O_2$	7	1.4		13
$\text{ClO}_{2}^{-} + \text{OH} \rightarrow \text{ClO}_{3}^{-} + \text{H}^{+}$	7	2.6		13
2 0	7	4.0	total rate, PR	12
	7	$3.5 \pm 0.5$	total rate, PR	this work
$ClO_2^- + OH \rightarrow ClO_2^+ + OH^-$		$7.9 \pm 0.4$	build-up of $ClO_2$ , FP	this work
	11	6.1	related to $k(OH + CO_3^{2-})$ , PR	9
	10	7.0	build-up of $ClO_2$ , PR	11

PR: pulse radiolysis; FP: (laser) flash photolysis.

'OH reacts with HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> to form the CO<sub>3</sub><sup>-</sup> radical anion with rate constants of  $8.5 \times 10^6$  and  $3.9 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, respectively.<sup>36</sup> Thus the total rate was  $1.9 \times 10^6$  s<sup>-1</sup>. Fig. 4 shows the absorption of CO<sub>3</sub><sup>--</sup> observed at 600 nm in the presence of different concentrations of CIO<sup>-</sup>. From the changes in the yield of CO<sub>3</sub><sup>--</sup>, the rate constant was determined to be  $(2.7 \pm 0.1) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, which is smaller than that determined by Buxton and Subhani<sup>9</sup> using the same method.

The rate constant for the reaction of 'OH with HClO was also determined by the competition method. Since the pK values of HClO and H<sub>2</sub>CO<sub>3</sub> are 7.52 and 6.4, respectively, at pH 5 HClO exists stably, although H<sub>2</sub>CO<sub>3</sub> is unstable because of its easy formation of CO<sub>2</sub> especially under N<sub>2</sub>O bubbling conditions. Thus, instead of the carbonate ion, HSO<sub>4</sub><sup>-</sup> was selected as the reactant for the competition. 'OH reacts with HSO<sub>4</sub><sup>-</sup> with a rate constant of 4.7 × 10<sup>5</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>,<sup>17</sup> to form the SO<sub>4</sub><sup>--</sup> radical anion, which has a peak absorption at 450 nm. The sample solution for irradiation included 1 mol dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub> and concentrations of NaClO varied between 0 and 10 × 10<sup>-3</sup> mol dm<sup>-3</sup>. The rate constant was determined from the changes in the maximum absorption of the SO<sub>4</sub><sup>--</sup> radical anion at 450 nm in the presence of different concentrations of HClO. In addition, HNO<sub>3</sub> was used as a competitor instead of HSO<sub>4</sub><sup>--</sup>. The 'OH radical reacts with HNO<sub>3</sub> with a rate constant of  $1.4 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1.16</sup> The solutions for irradiation contained 3 mol dm<sup>-3</sup> of HClO<sub>4</sub>, 0.015 mol dm<sup>-3</sup> of HNO<sub>3</sub> and different concentrations of HClO. The rate constant for the reaction of 'OH with HClO was determined from the absorbance changes of the NO<sub>3</sub>' radical at 635 nm. The rate constant was determined to be  $(1.4 \pm 0.1) \times 10^8$  or  $(1.1 \pm 0.2) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> from the HSO<sub>4</sub><sup>-</sup> or HNO<sub>3</sub> competition method, respectively. The two results are consistent. As can be seen, HClO reacts with 'OH with a rate of one order less than that of ClO<sup>-</sup> with 'OH.

Reactions of oxychlorides with 'OH and the rate constants are listed in Table 3. The 'OH radical is a powerful oxidant, having a standard reduction potential of 2.7 V in acidic solution and 1.8 V in neutral solution, as summarized in Table  $1.^{12,37,38}$  The reaction of 'OH with oxychloride ions can be thought of as a simple electron transfer,

$$OH + ClO_x^n \to ClO_x^{n-1} + OH^-$$
(II)

where *n* is the charge on the ion, although Erikson *et al.* suggested that, in the case of reaction of 'OH with  $ClO_2^-$ , both electron transfer and adduct formation occurs. The adduct was probably a peroxide (HOClO<sub>2</sub><sup>--</sup>), which can react with excess  $ClO_2^-$  to form  $ClO_2^{.11}$ 

**Table 4** Rate constants for reactions of oxychlorides with  $SO_4$  radical (10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>)

reaction	pH	rate constant, k	comments	ref.
$Cl^- + SO_4^{-} \rightarrow Cl^+ + SO_4^{2-}$		0.36 + 0.01	I = 1.5, decay 500 nm, FP	this work
· · · ·		0.19 + 0.01	$I \rightarrow 0$ , from k at $I = 1.5$	
	2–3	0.01	build-up at 340 nm, FP	55
	6.2	0.47	I = 0.1, decay at 500 nm, FP	56
		0.27	$I \rightarrow 0$ , from k at $I = 0.1$	
		0.25	$I \rightarrow 0$ , decay at 500 nm, FP	57
		0.27	$I \rightarrow 0$ , decay at 480 nm, FP	44
	1.5	0.26	$I \rightarrow 0$ , decay at 510 nm, FP	58
	1.4	0.2	I = 0.2, decay at 480 nm, PR	59
		0.13	I = 0.056, build-up of Cl <sub>2</sub> <sup>-</sup> , PR	18
	6.8	0.31	I = 0.007, decay at 480 nm, PR	43
		0.26	$I \rightarrow 0$ , from k at $I = 0.007$	
$HClO + SO_4^{-} \rightarrow ClO^{-} + HSO_4^{-}$	0	$0.011 \pm 0.001$	PR of 1 mol dm <sup><math>-3</math></sup> H <sub>2</sub> SO <sub>4</sub>	this work
$\text{ClO}^- + \text{SO}_4^{-} \rightarrow \text{ClO}^+ + \text{SO}_4^{2-}$		$6.6 \pm 0.5$	I = 6, PR of 2 mol dm <sup>-3</sup> Li <sub>2</sub> SO <sub>4</sub>	this work
		$1.3 \pm 0.1$	$I \rightarrow 0$ , from k at $I = 6$	
$\text{ClO}_2^- + \text{SO}_4^- \rightarrow \text{ClO}_2^+ + \text{SO}_4^2^-$		$2.6 \pm 0.1$	I = 0.03, PR	this work
		$1.9 \pm 0.1$	$I \rightarrow 0$ , from k at $I = 0.03$	
		$2.4 \pm 0.1$	I = 0.15,  FP	this work
		$1.3 \pm 0.1$	$I \rightarrow 0$ , from k at $I = 0.15$	
	3.1	$3.4 \pm 0.3$	I = 1.6, related to	this work
			$k(SO_4 + NO_3), FP$	
$a_1 a_2 = a_1 a_2 a_2 a_3 a_4 a_5 a_5 a_2 a_5 a_5 a_5 a_5 a_5 a_5 a_5 a_5 a_5 a_5$	2.2	$0.92 \pm 0.08$	$I \rightarrow 0$ , from k at $I = 1.6$	15
$ClO_3 + SO_4^{-1} \rightarrow ClO_3^{-1} + SO_4^{-2}^{-1}$	3.3	$0.008 \pm 0.001$	I = 0.6, FP	15
		$0.004 \pm 0.0005$	$I \rightarrow 0$ , from k at $I = 0.6$	

FP: (laser) flash photolysis; PR: pulse radiolysis.

Table 5 Rate constants for reactions of oxychlorides with NO<sub>3</sub> radical ( $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )

reaction	pН	rate constant, k	comments	ref.
$Cl^- + NO_3 \rightarrow Cl^+ + NO_3^-$	0	$(9.1 \pm 0.3) \times 10^{-3}$	decay at 635 nm, FP	this work
	8.3–9.0	$9.3 \times 10^{3}$	decay at 633 nm conversion from $SO_4$ ., FP	47
		0.071	build-up at 345 nm, decay at 640 nm, PR of 5 mol $dm^{-3}$ NaNO <sub>3</sub>	60
		0.1	build-up at 345 nm, PR of 2 mol $dm^{-3}$ NO $-$	18
$\text{HClO} + \text{NO}_3$ $\rightarrow$ $\text{ClO}$ $+$ $\text{HNO}_3$	<0	$0.043 \pm 0.001$	decay at 635 nm, PR of 0.015 mol dm <sup><math>-3</math></sup> HNO <sub>2</sub>	this work
$\text{ClO}^- + \text{NO}_3^- \rightarrow \text{ClO}^+ + \text{NO}_3^-$		$3.6 \pm 0.2$	decay at 635 nm PR of 5 mol dm <sup><math>-3</math></sup> NaNO <sub>2</sub>	this work
$\text{ClO}_2^- + \text{NO}_3^- \rightarrow \text{ClO}_2^- + \text{NO}_3^-$	3.1	$4.1 \pm 0.3$	decay at 633 nm,	this work
$\text{ClO}_3^- + \text{NO}_3^- \rightarrow \text{ClO}_3^- + \text{NO}_3^-$	0	$(1.0 \pm 0.1) \times 10^{-5}$	decay at 633 nm, FP	15

FP: (laser) flash photolysis; PR: pulse radiolysis.

Such a simple electron transfer step is unlikely in the oxidation of halide and pseudo-halide ions, because of the large solvent reorganization energy involved in forming the hydrated hydroxide ion. Instead, it is suggested<sup>39,40</sup> that an intermediate adduct is formed.

$$OH + X^{-} \rightarrow HOX^{-}$$
 (III)

When X = Cl, the rate constant was determined to be  $4.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^{41} \text{ or } 3.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^{42} \text{ In}$  acidic conditions, HOX<sup>-</sup> reacts with H<sup>+</sup> and the halide atom leading to formation of the dihalide radical anion. Reaction of 'OH with ClO<sub>2</sub>' is also complicated. Disproportionation of ClO<sub>2</sub>' leads to the formation of HClO and ClO<sub>3</sub><sup>-12,13</sup>

## 3.3 Reactions with SO<sub>4</sub><sup>.-</sup>, NO<sub>3</sub><sup>.</sup> and Cl<sub>2</sub><sup>.-</sup> (Cl<sup>.</sup>) radical

**3.3.1 Reactions with SO<sub>4</sub>.**<sup>--</sup>. The reactions of SO<sub>4</sub>.<sup>-</sup> and their rate constants are listed in Table 4. There have been many reports of the rate constant for the reaction between SO<sub>4</sub>.<sup>-</sup> and Cl<sup>-</sup> to yield Cl<sup>-</sup> and then the Cl<sub>2</sub>.<sup>-</sup> radical anion. SO<sub>4</sub>.<sup>-</sup> and Cl<sub>2</sub>.<sup>-</sup> radical anions have molar absorption coefficients of 1600 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at 450 nm<sup>17,43,44</sup> and 8800 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> at 340 nm,<sup>41</sup> respectively. In this work, SO<sub>4</sub>.<sup>-</sup> was produced from the KrF laser photolysis of peroxodisulfate ion (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>). Both the build-up of Cl<sub>2</sub>.<sup>-</sup> and the decay of SO<sub>4</sub>.<sup>-</sup> were observed in the presence of Cl<sup>-</sup>. The rate constant was determined from the decay kinetics of SO<sub>4</sub>.<sup>-</sup> at 500 nm, to avoid any contribution to the absorption decay



**Fig. 5** Transient absorbance of NO<sub>3</sub><sup>•</sup>, observed at 635 nm, from the laser photolysis of solutions of 0.2 mol dm<sup>-3</sup> (NH<sub>4</sub>)S<sub>2</sub>O<sub>8</sub>, 1 mol dm<sup>-3</sup> NaNO<sub>3</sub> and (a) 0, (b)  $1.1 \times 10^{-5}$ , (c)  $2.3 \times 10^{-5}$  and (d)  $4.6 \times 10^{-5}$  mol dm<sup>-3</sup> NaClO<sub>2</sub>. The solid lines are the FACSIMILE curves.

from the tail of the Cl<sub>2</sub><sup>--</sup> radical anion. The results,  $(3.6 \pm 0.1) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 0.15 and  $(1.9 \pm 0.1) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, corrected at  $I \rightarrow 0$ , were consistent with most of the previously reported data.

Since  $S_2O_8^{2-}$  was observed to react with HClO and ClO<sup>-</sup>, for its reaction with HClO, SO<sub>4</sub><sup>.-</sup> was produced by reaction of 'OH with 1 mol dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub>; and for its reaction with ClO<sup>-</sup>, it was produced from the direct action of radiation in 2 mol dm<sup>-3</sup> of Li<sub>2</sub>SO<sub>4</sub>, which has a  $G(-SO_4^{2-})$  value of 3.0, determined previously in our laboratory.<sup>17</sup>  $G(SO_4^{.-})$  is related to  $G(-SO_4^{2-})$  and the electron fraction of the solute in solution. Rate constants were determined from the decay kinetics of SO<sub>4</sub><sup>.-</sup> at 450 nm. SO<sub>4</sub><sup>.-</sup> reacts rapidly with ClO<sup>-</sup> (1.3 × 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 0) but relative slowly with HClO (1.1 × 10<sup>7</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>). For reaction with ClO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>.-</sup> was generated from the

For reaction with  $\text{ClO}_2^-$ ,  $\text{SO}_4^{--}$  was generated from the photolysis of  $\text{S}_2\text{O}_8^{2-}$  or pulse radiolysis *via* its reaction with  $e_{aq}^-$ . The  $\text{ClO}_2^-$  radical was observed, from the reaction of  $\text{SO}_4^{--}$  with  $\text{ClO}_2^-$ . The rate constant of the reaction was determined from the decay kinetics at 500 nm; values of  $1.3 \times 10^9$  and  $1.9 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> were deduced from photolysis or radiolysis, respectively.

In our previous paper<sup>15</sup> reaction of SO<sub>4</sub><sup>--</sup> with ClO<sub>3</sub><sup>-</sup> to form ClO<sub>3</sub><sup>-</sup> radical, was observed by laser photolysis. The rate constant was determined to be  $(4.0 \pm 0.5) \times 10^6$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> from simulation.

**3.3.2 Reactions with NO<sub>3</sub>**. The reactions of the NO<sub>3</sub> radical and their rate constants are listed in Table 5. For reaction with Cl<sup>-</sup>, the NO<sub>3</sub> radical was produced conveniently by the XeF laser photolysis of the complex of cerium(v) and nitrate in the presence of nitric acid.<sup>45,46</sup> The rate constant was determined from the decay kinetics of the radical at around 635 nm. There has been considerable disagreement about the rate constant for this reaction. It has been suggested<sup>47</sup> that this difference might be due to a secondary ionic strength effect which is known to influence the reaction rate of ion–dipole reactions.

Since HClO and ClO<sup>-</sup> were observed to react with cerium(IV) ions, NO<sub>3</sub><sup>-</sup> radical was produced by pulse radiolysis *via* reaction of 'OH with nitric acid for its reaction with HClO, and by the direct radiation of concentrated solution of NaNO<sub>3</sub> for its reaction with ClO<sup>-</sup>. For radiation of nitrate,  $G(-NO_3^-) = 4.8$  has been determined previously in our laboratory.<sup>16</sup> Like SO<sub>4</sub><sup>--</sup>, the NO<sub>3</sub><sup>-</sup> radical reacts rapidly with ClO<sup>-</sup> (3.6 × 10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) but relatively slowly with HClO (4.3 × 10<sup>7</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>).

For reaction of  $\text{ClO}_2^-$ , because of its instability in strong acid solution (the pK value of HClO<sub>2</sub> is *ca.* 2.5), NO<sub>3</sub><sup>•</sup> was produced by reaction of SO<sub>4</sub><sup>•-</sup> with 1 mol dm<sup>-3</sup> of NO<sub>3</sub><sup>-</sup>.

Fig. 5 shows the absorbance of NO<sub>3</sub><sup>•</sup> at 635 nm in the presence of different concentrations of ClO<sub>2</sub><sup>-</sup>. As can be seen, the decay of NO<sub>3</sub><sup>•</sup> increased, but its maximum absorbance decreased, as the concentration of ClO<sub>2</sub><sup>-</sup> increased. It was concluded that reaction of SO<sub>4</sub><sup>•-</sup> with NO<sub>3</sub><sup>•</sup> and ClO<sub>2</sub><sup>-</sup>, and reaction of NO<sub>3</sub><sup>•</sup> with ClO<sub>2</sub><sup>-</sup> had occurred simultaneously. From the decay kinetics at 635 nm, the rate constant of the reaction of NO<sub>3</sub><sup>•</sup> with ClO<sub>2</sub><sup>-</sup> was determined to be  $(4.1 \pm 0.3) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. The rate constant of SO<sub>4</sub><sup>•-</sup> with ClO<sub>2</sub><sup>-</sup> was deduced to be  $(3.4 \pm 0.3) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 1.6 from simulation in which the rate constant of SO<sub>4</sub><sup>•-</sup> with NO<sub>3</sub><sup>-</sup> was set to be  $2.0 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 1.6, deduced from the value of  $5.0 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at  $I \rightarrow 0$  by eqn. (1).<sup>47</sup>

In the previous paper,<sup>15</sup> the equilibrium reaction of NO<sub>3</sub><sup>-</sup> with  $\text{ClO}_3^-$  was observed by laser photolysis. From the rate constants determined for the forward and reverse reaction, the reduction potential of  $\text{ClO}_3^-$  radical was measured to be 2.35 V vs. NHE.

3.3.3 Reactions with Cl<sub>2</sub> (Cl<sup>·</sup>). The reactions of Cl<sub>2</sub><sup>·-</sup> (Cl<sup>·</sup>) and their constants are listed in Table 6.  $Cl_2^{-}$  is formed from reaction of Cl<sup>°</sup> with Cl<sup>-</sup> with a stability constant of  $1.9 \times 10^5$  dm<sup>3</sup> mol<sup>-1.41</sup> Such a high value implies that Cl<sup>°</sup> are unlikely to be chemically significant, except in very dilute solutions of chloride ion in water. Thus only a few rate constants for the reactions of Cl' in water have been obtained, compared with the wealth of data that is available on the reactions of Cl<sub>2</sub><sup>·-</sup>. Cl<sup>·</sup> can be produced through the formation of an adduct of 'OH with Cl<sup>-</sup> followed by reaction of the adduct (HOCl<sup>--</sup>) with H<sup>+</sup> in acidic conditions. Since, in acid solution, HClO reacts with HCl to reform Cl<sub>2</sub>, for its reaction with ClO<sup>-</sup>, Cl<sub>2</sub><sup>--</sup> was produced by direct radiation in concentrated solutions of LiCl. Many investigations have been carried out on the production of dihalide radical anions in the radiolysis of concentrated solutions of halide ions.<sup>18-21</sup> From the decay at 340 nm, the rate constant of  $Cl_2$ <sup>--</sup> with  $ClO^$ was determined to be  $(5.4 \pm 0.3) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 5.

The same method was used to study the reaction of  $\text{Cl}_2^{-1}$  with  $\text{ClO}_2^{-1}$ . In addition, the reaction was also observed using KrF photolysis to generate Cl<sup>-</sup> and then  $\text{Cl}_2^{--}$ , by reaction of SO<sub>4</sub><sup>--</sup> with Cl<sup>-</sup>. Absorption due to ClO<sub>2</sub><sup>-</sup> was observed after the reaction was completed. The rate constant for the reaction was determined to be  $(1.3 \pm 0.1) \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 5, from pulse radiolysis, or  $(3.5 \pm 0.2) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at I = 0.25, from laser photolysis. Their corrected values at  $I \rightarrow 0$  are comparable.

Kläning and Wolff<sup>48</sup> have reported the rate constants for the reactions of Cl with HClO and ClO<sup>-</sup>. The radical was produced by the photolysis of solutions of HClO and ClO<sup>-</sup>; however, a detailed description of the calculation of the rate constants was not given in that paper. It can be seen, from Table 6, that Cl reacts with HCl and ClO<sup>-</sup> more rapidly than Cl<sub>2</sub><sup>-</sup> owing to the relative higher reduction potential of the former radical. Recently, a new value of  $K = 4.7 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> for Cl<sub>2</sub><sup>--</sup> was reported by Adams *et al.*,<sup>49</sup> which is 40 times lower than the generally accepted value. This low value of K makes it possible to measure the rates of reaction of Cl<sup>-</sup> using pulse radiolysis.

In general, free radicals R', including 'OH,  $SO_4$ '',  $NO_3$ ' and  $Cl_2$ '' (Cl'), react with oxychloride ions *via* an electron-transfer mechanism, leading to the formation of oxychloride radicals,

$$\mathbf{R}^{\cdot} + \mathbf{ClO}_{x}^{-} \to \mathbf{R}^{-} + \mathbf{ClO}_{x}^{\cdot}$$
(IV)

where x = 0, 1, 2, or 3. As can be seen from Table 1, since  $\Delta E$  between **R**<sup>•</sup> and ClO<sub>x</sub><sup>•</sup> (x = 1, 2) is more positive than 0.4 V, the electron transfer will be complete. Furthermore, these reactions occur with nearly diffusion-controlled rate constants (>10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>).

### 4 Conclusion

Free radicals, including  $e_{aq}^{-}$ , 'OH, SO<sub>4</sub><sup>·-</sup>, NO<sub>3</sub><sup>·</sup> and Cl<sub>2</sub><sup>·-</sup> (Cl') were generated by various pulse radiolysis and laser photolysis methods in order to determine the rate constants for their reactions with oxychloride compounds. Most of the reactions have nearly diffusion-controlled rate constants (>10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>). ClO<sup>-</sup> has relatively higher reactivity than its acid form, HClO.  $e_{aq}^{-}$  reacts with the oxychlorides to form their electron adducts which dissociate easily. Interconversion reactions occur between 'OH, SO<sub>4</sub><sup>·-</sup>, NO<sub>3</sub><sup>·</sup>, and Cl<sub>2</sub><sup>·-</sup> (Cl') radicals and the oxychloride ions, *via* an electron-transfer mechanism. The kinetics results obtained here will be used in our future simulation work to understand the radiationinduced reactions taking place in groundwater, which is relevant to geological studies on radioactive waste disposal. These reactions may also be suggested to play potential roles in the chemistry of the atmospheric aqueous phase.

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reaction	pH	rate constant, k	comments	ref.
$Cl^- + Cl^- \rightleftharpoons Cl_2^{}$		6.5	build-up at 360 nm, FP of ClO <sup>-</sup>	48
-	3.5	8	build-up of $Cl_2$ .	61
	2	21	$K = 1.9 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ fitting at 340 nm. PR	41
			$K = 4.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$	49
$HClO + Cl \rightarrow ClO + HCl$		3	no detail, FP of HClO	48
$ClO^- + Cl^- \rightarrow ClO^- + Cl^-$		8.2	no detail, FP of ClO <sup>-</sup>	48
$\text{ClO}^- + \text{Cl}_2^- \rightarrow \text{ClO}^+ + 2\text{Cl}^-$		$0.54 \pm 0.03$	I = 5, decay at 340 nm PR of 5 mol dm <sup>-3</sup> LiCl	this work
		$0.11 \pm 0.01$	$I \rightarrow 0$ , from k at $I = 5$	this work
$\text{ClO}_2^- + \text{Cl}_2^- \rightarrow \text{ClO}_2^+ + 2\text{Cl}^-$		$1.3 \pm 0.1$	I = 5, decay at 340 nm, PR of 5 mol dm <sup>-3</sup> LiCl	this work
		$0.25 \pm 0.02$	$I \rightarrow 0$ , from k at $I = 5$	this work
		$0.35 \pm 0.02$	I = 0.25, decay at 340 nm, conversion from SO <sub>4</sub> <sup></sup> , FP	this work
		$0.16\pm0.01$	$I \rightarrow 0$ , from k at $I = 0.25$	this work

**Table 6** Rate constants for reactions of oxychlorides with  $Cl_2^{-}$  (Cl') radical (10<sup>9</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>)

FP: (laser) flash photolysis; PR: pulse radioysis.

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