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Temperature dependence of the rate constant for the bimolecular recombination of Cl_2^- in water—A pulse radiolysis study

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HIGHLIGHTS

- The activation energy for $k(Cl_2^- + Cl_2^-)$ is 10.89 ± 0.37 kJ mol^{-1} over 22–87 °C.
- The activation energy is less than expected for a diffusion-controlled reaction.
- The good fit to $1/k_{obs} = 1/k_{diff} + 1/k_{react}$ with $k_{react} = A'T$ is found.
- $2k(Cl_2^- + Cl_2^-) = 2 \times (8.7 \times 10^8)$ M^{-1} s^{-1} for body temperature (37 °C) and pH 7.4.

ARTICLE INFO

ABSTRACT

The rate constant for the disproportionation of Cl_2^- in water has been determined for the temperature range 22–87 °C using pulse radiolysis of 0.1 M NaCl + 1 mM HClO$_4$ aqueous solution. The rate constant for the decay of Cl_2^- has been found to be $2 \times (7.35 \pm 0.53) \times 10^8$ M^{-1} s^{-1} at 22 °C (at zero ionic strength). The determined activation energy, $E_a = 10.89 \pm 0.37$ kJ mol^{-1}, is less than expected for diffusion-controlled reactions. A good fit to the Noyes equation ($1/k_{obs} = 1/k_{diff} + 1/k_{react}$) has been obtained assuming the reaction step is activationless with $k_{react} = A'T$.

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1. Introduction

The radical anion Cl_2^- is a transient oxidant formed in aqueous solutions containing chloride ions and OH radicals (Jayson et al., 1973) or SO_4^- ions (Chawla and Fessenden, 1975). Therefore, data on the rate constants of Cl_2^- reactions are necessary to model the impact of chloride ions on chemical reactions occurring in the atmosphere, living organisms and water cooling systems. In the primary heat transport systems of water-cooled nuclear power reactors, trace impurities like chloride ions may influence hydrogen generation because they produce Cl_2^- ions *via* reactions with OH radicals, formed in the radiolysis of the coolant. In order to assess the effects due to Cl^- impurity it is necessary to have data on the rate constants of reactions involving Cl^- and Cl_2^- ions for elevated temperatures.

In the present study we focus on the disproportionation reaction of Cl_2^-:

$$Cl_2^- + Cl_2^- \rightarrow Cl_2 + 2Cl^- \tag{1}$$

The published values of $2k_1$ have been measured at room temperature by following the decay of the absorption at 340 nm using pulse radiolysis (Lierse et al., 1987; Ershov et al., 2002) or laser-flash photolysis (McElroy, 1990; Huie and Clifton, 1990). McElroy (1990) monitored the decay of Cl_2^- at 340 nm following the photolysis of $K_2S_2O_8$ in the presence of NaCl and reported $2k_1^0 = (1.4 \pm 0.2) \times 10^9$ M^{-1} s^{-1} for 20 °C and zero ionic strength ($I = 0$). Huie and Clifton (1990) examined the effect of the concentration of chloride ions for various values of the ionic strength (I) showing a slight decrease in $2k_1$ corrected to $I = 0$ as the chloride ion concentration is increased. Assuming $\varepsilon_{340} = 8800$ M^{-1} cm^{-1} they obtained an average $2k_1^0 = 1.3 \times 10^9$ M^{-1} s^{-1} at 24.3 °C and $I = 0$. This value is in reasonable agreement with the later determination, $2k_1 = 2.6 \times 10^9$ M^{-1} s^{-1}, in 1 M NaCl solution at pH 3.3 (Ershov et al., 2002), which corrected to $I = 0$ gives $2k_1^0 \sim 1.13 \times 10^9$ M^{-1} s^{-1}.

The literature data on $2k_1^0$ suggest that the bimolecular recombination of dichloride ions is diffusion controlled at room temperature. In this paper we report our measurements of k_1 for the temperature range 22–87 °C obtained using kinetic spectroscopy in pulse radiolysis experiments. We will show that the activation energy is less than expected for diffusion-controlled reactions.
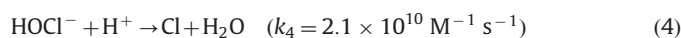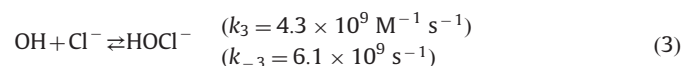
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2. Experimental section

The kinetics of reaction (1) have been determined by measuring the decay of Cl_2^- in an irradiated aqueous solution containing 0.1 M NaCl and 1 mM $HClO_4$. All the chemical compounds used for the experiments were of the purest commercially available grade and were used as received. Perchloric acid ($HClO_4$) and sodium chloride (NaCl) were purchased from Sigma-Aldrich. A solution containing 0.1 M NaCl and 1 mM $HClO_4$ was prepared with Millipore water. The solution was subsequently deoxygenated by purging with high purity N_2O. At 20 °C the saturation concentration of $N_2O \approx 2.5 \times 10^{-2}$ M. Pulse radiolysis experiments with UV–vis detection was performed with 17 ns pulses of high-energy electrons from the Lodz University of Technology 6 MeV ELU-6 linear accelerator. A description of the pulse radiolysis setup and data collection system is given elsewhere (Karolczak et al., 1992). Absorbed dose was of the order of 53–57 Gy per pulse as measured at room temperature using N_2O-saturated 0.01 M solution of potassium thiocyanate (KSCN) as the dosimeter, and taking $G\varepsilon_{475} = 5.28 \times 10^{-4}$ m^2 J^{-1} (Buxton and Stuart, 1995).

In N_2O-saturated solution hydrated electrons (e_{aq}^-) are quickly converted into OH radicals according to Eq. (2) (Schuler and Janata, 1982):

$$e_{aq}^- + N_2O(+H_2O) \rightarrow N_2 + OH + OH^- \quad (k_2 = 9.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \quad (2)$$

where the reaction rate constant refers to the ambient conditions. In the presence of H^+ and Cl^- ions OH radicals are converted into Cl_2^- in the following steps (Jayson et al., 1973):

$$OH + Cl^- \rightleftharpoons HOCl^- \quad \begin{matrix} (k_3 = 4.3 \times 10^9 \text{ M}^{-1}\text{ s}^{-1}) \\ (k_{-3} = 6.1 \times 10^9 \text{ s}^{-1}) \end{matrix} \quad (3)$$

$$HOCl^- + H^+ \rightarrow Cl + H_2O \quad (k_4 = 2.1 \times 10^{10} \text{ M}^{-1}\text{ s}^{-1}) \quad (4)$$

$$Cl + Cl^- \rightarrow Cl_2^- \quad (k_5 = 2.1 \times 10^{10} \text{ M}^{-1}\text{ s}^{-1}) \quad (5)$$

The rate constant k for the formation of Cl_2^- at room temperature is of the order of 9.2×10^5 s^{-1} as estimated from Eq. (6) using the concentrations of chloride and hydrogen ions $c_{Cl^-} = 0.1$ M, $c_{H^+} = 1$ mM, and the activation coefficients, $\gamma_{Cl^-} = 0.778$, $\gamma_{H^+} = 0.796$.

$$k = \frac{k_3 k_4 \gamma_{Cl^-} c_{Cl^-} \gamma_{H^+} c_{H^+}}{k_{-3} + k_4 \gamma_{H^+} c_{H^+}} \quad (6)$$

All experiments were carried out by pulse radiolysis coupled with optical detection at 340 nm, being the absorption maximum of Cl_2^-. The optical path of the cell was 1 cm. The optical absorption from Cl_2^- was recorded at 340 nm using a monochromator ARC SpectraPro275, a photomultiplier R 928 Hamamatsu Photonics and an oscilloscope Tektronix TDS 540 MHz. At 340 nm only Cl_2^- gives rise to the absorption (Jayson et al., 1973). Measurements were made for the temperature range 22–87 °C. The quartz cell containing the prepared solution was thermostated for 10 min and then irradiated. Up to 50 °C the uncertainty in the temperature was 0.1 °C. Above 50 °C a temperature of the sample might be lower than recorded by at most 2.0 °C. This uncertainty has been included in the data analysis. The Cl_2^- molar absorption coefficient $\varepsilon_{340} = 9600$ M^{-1} cm^{-1} revised by Buxton and co-workers (Adams et al., 1995) for ambient conditions was assumed also for higher temperatures. At each temperature we recorded and analysed 3–7 independent traces.

3. Results and data analysis

The change of the total absorbance of Cl_2^- with time after an electron pulse was measured at 340 nm over the temperature range 22–87 °C. Typical data taken are shown in Fig. 1. Assuming that the initial decay of Cl_2^- is determined by reaction (1) we fitted the signals tracked between 10 and 30 μs to second-order kinetics. The obtained values of the correlation coefficient were of the order of 0.994. Fitted curves are displayed in Fig. 1. The data collected for all temperatures were recalculated to k_1 using $\varepsilon_{340} = 9600$ M^{-1} cm^{-1} (Adams et al., 1995) and corrected to zero ionic strength (k_1^0) following Eq. (7), resulting from the transition state theory for the like-charged reactants ($Z_A = Z_B = -1$):

$$\log \frac{k_1}{k_1^0} = \log \gamma_{\pm}^2 \quad (7)$$

Since the mean activation coefficient $\gamma_{\pm}$ depends on temperature we have employed the Debye–Hückel extended law (see Swiatla-Wojcik, 2008) to scale with temperature the tabulated ambient value, $\gamma_{\pm(298)} = 0.778$:

$$\gamma_{\pm(T)} = \gamma_{\pm(298)} \times \frac{A\sqrt{I} / (1+B\sqrt{I})}{A_{298}\sqrt{I} / (1+B_{298}\sqrt{I})} \quad (8)$$

where $A = 1.825 \times 10^6/(\varepsilon \times T)^{3/2}$, $B = 150.87/(\varepsilon \times T)^{1/2}$, T is absolute temperature, ε is the dielectric constant of the solvent, and A_{298}, B_{298} denote A, B coefficients calculated for 298 K. The dielectric constant of water has been calculated using the empirical formula given by Fernandez et al. (1997). The corrected rate constants (k_1^0) are listed in Table 1 and displayed in Fig. 2 as a function of absolute temperature. For 22 °C we obtained $k_1^0 = (7.35 \pm 0.53) \times 10^8$ M^{-1} s^{-1}, in good agreement with the literature data on $2k_1^0$ multiplied by 0.917 due to the difference in ε_{340} (McElroy, 1990; Huie and Clifton, 1990; Ershov et al., 2002).

The values of k_1^0 obtained as a function of temperature have been modelled by the Arrhenius equation

$$k_1^0 = Ae^{-(E_a/RT)} \quad (9)$$

where R is the Universal gas constant, T is the absolute temperature, and the pre-factor (A) and the activation energy (E_a) are fitted parameters. Using OriginPro 9.0 software we have performed non-linear regression assigning weights to the rate constants and temperatures according to their uncertainties. The correlation coefficient of 0.990 has been obtained. The adjusted values of the pre-factor and the activation energy are $A = (5.95 \pm 0.81) \times 10^{10}$ M^{-1} s^{-1} and $E_a = 10.89 \pm 0.37$ kJ mol^{-1}. Using these parameters we estimate $2k_1 = 2 \times (8.7 \times 10^8)$ M^{-1} s^{-1} at body temperature (37 °C) and pH 7.4.
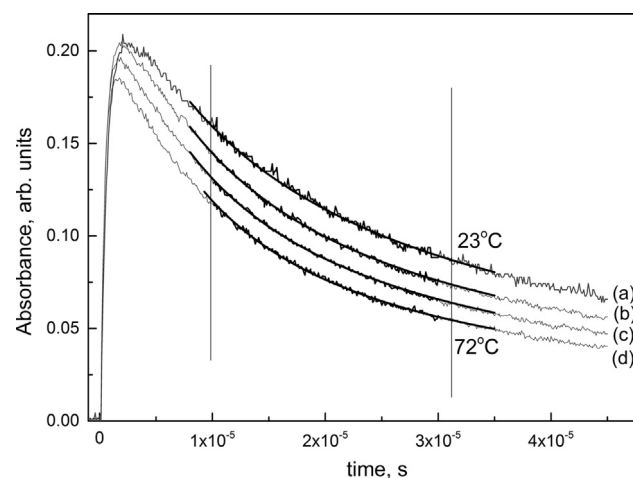

Fig. 1. Decay of the Cl_2^- absorption in N_2O saturated aqueous solution containing 0.1 M NaCl and 1 mM $HClO_4$ after the 17 ns electron pulse measured at: (a) 23 °C (b) 39 °C, (c) 55 °C, (d) 72 °C. The signals were acquired at 340 nm. Fits are superimposed as solid lines.

Table 1
Rate constants for reaction (1) at zero ionic strength and the standard deviations for selected temperatures within the measured range 22–87 °C.

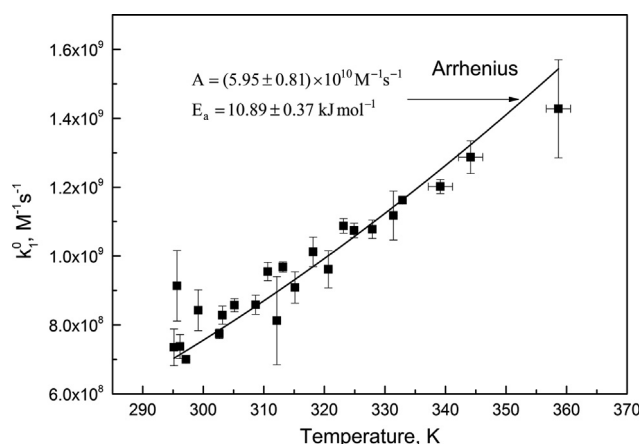| Temperature (°C)	$k_1^0 \times 10^{-8}$ ($M^{-1} s^{-1}$)
22.0 ± 0.1	7.35 ± 0.53
30.0 ± 0.1	8.28 ± 0.26
37.5 ± 0.1	9.55 ± 0.27
45.0 ± 0.1	10.12 ± 0.43
50.0 ± 0.1	10.88 ± 0.21
58.3 ± 0.5	11.18 ± 0.71
66.0 ± 1.0	12.02 ± 0.20
71.0 ± 1.0	12.87 ± 0.47
85.5 ± 1.0	14.28 ± 1.42

Fig. 2. Rate constant for reaction (1) as a function of temperature. The solid line shows the nonlinear regression fit to Eq. (9) (the correlation coefficient is 0.990), Arrhenius parameters and the standard errors of the regression are displayed.

Fig. 3. Temperature dependence for the rate constant of reaction (1) calculated from the Noyes Eq. (12). Also shown are k_{diff} from Eq. (10) and $k_{\text{react}} = A'T$.

4. Discussion

The ambient value of $2k_1^0$ suggests that the decay of dichloride ions *via* bimolecular recombination is diffusion controlled. To calculate an activation energy expected for the rate constant of diffusion controlled reaction (k_{diff}) we use the Smoluchowski equation, which for reaction (1) can be written as (e.g. see Swiatla-Wojcik and Buxton, 1995, Swiatla-Wojcik, 2013):

$$k_{\text{diff}} = 8\pi N_{\text{Av}} D_{Cl_2^-} r_{Cl_2^-} \beta \times f_D$$
$$f_D = \frac{e^2/(8\pi\varepsilon_0\varepsilon\, r_{Cl_2^-}\, k_B T)}{\exp[e^2/(8\pi\varepsilon_0\varepsilon\, r_{Cl_2^-}\, k_B T)] - 1} \tag{10}$$

where N_{Av} is the Avogadro number, $D_{Cl_2^-}$ is the diffusion coefficient, and $r_{Cl_2^-}$ is the reaction radius of Cl_2^-, e is the elementary charge, k_B is the Boltzmann constant, and ε_0 is the permittivity of free space. The statistical spin factor $\beta = 1$ was assumed by analogy with OH radical (Buxton and Elliot, 1993). For the studied range of temperature we do not expect any change in β, and the Debye factor f_D decreases by ca. 18% due to the decrease in ε. We obtain 15 kJ mol^{-1} (see Fig. 3) for the activation energy of k_{diff} at zero ionic strength, taking the water viscosity η from Sengers and Watson (1986) and estimating the temperature dependence of $D_{Cl_2^-}$ from the Stokes–Einstein equation:

$$D_{Cl_2^-} = \frac{k_B}{a\pi r_h} \times \frac{T}{\eta} \tag{11}$$

where r_h is the hydrodynamic radius of Cl_2^-, and the coefficient a equals 4 if r_h is comparable with the size of the water molecule (see Swiatla-Wojcik, 2013). Hence, the observed increase of k_1^0 with temperature is slower than expected for the diffusion-controlled recombination.
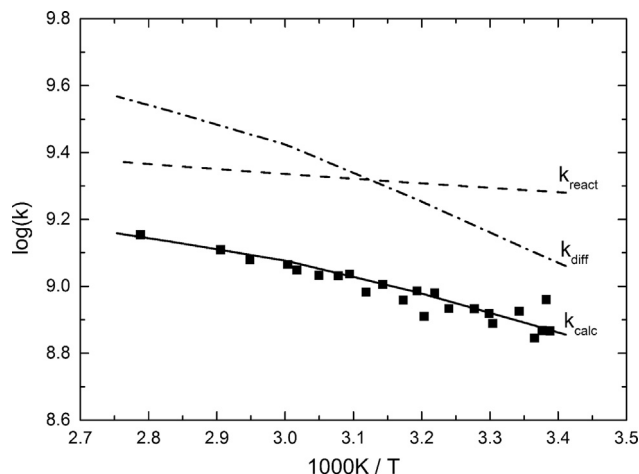
Reaction (1) is another example of the combination of two free radicals. The temperature dependence of the rate constants for such reactions was analysed by Elliot et al. (1990), Buxton and Elliot (1993), Buxton and Stuart (1997), Buxton et al. (1998b)) using the Noyes relation:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{diff}}} + \frac{1}{k_{\text{reat}}} \tag{12}$$

with $k_{\text{react}} = A'T$ for the chemical reaction part. This activationless form for the chemical step describes the temperature dependence of radical–radical recombination rate constants very well. Treating our kinetic data (k_{obs}) in the same way we have matched the experimental points (see k_{calc} in Fig. 3), assuming $A' = 6.50 \times 10^6$ M^{-1} s^{-1}K^{-1}, $r_{Cl_2^-} = 0.185$ nm and $r_h = 0.26$ nm, $a = 4$ in Eq. (11). The good fit indicates that, although the stability constant of Cl_2^- is very large, $(1.4 \pm 0.1) \times 10^5$ M^{-1}, (Buxton et al., 1998a), the rate of reaction (1) is much the same as the rate of recombination of neutral radicals (OH + OH, H + OH, NH$_2$ + NH$_2$, OD + OD, D + OD). As was pointed out by Buxton and Elliot (1993) it is not possible to calculate A' for a reaction in solution without a precise knowledge of the relevant partition functions. The coefficient A' obtained for the bimolecular recombination of Cl_2^- is lower compared to the value of 3.7×10^7 M^{-1} s^{-1} assumed for OH + OH (Swiatla-Wojcik and Buxton, 1995). This difference is consistent with a decrease in the activation entropy due to electrostatic interaction in the case of $Cl_2^- + Cl_2^-$. The value of 1.41×10^{-9} m^2 s^{-1} obtained for $D_{Cl_2^-}$ at 25 °C is slightly higher than 1.38×10^{-9} m^2 s^{-1} reported for the diffusion of chlorine (Cl$_2$) in water (Tang and Sandall, 1985).

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