

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/280974668>

# Temperature dependence of the rate constant for hydrogen atom reaction with $\text{Cl}_2-\bullet$ in water by pulse radiolysis of aqueous HCl solution

ARTICLE *in* RADIATION PHYSICS AND CHEMISTRY · NOVEMBER 2015

Impact Factor: 1.38 · DOI: 10.1016/j.radphyschem.2015.07.007

---

READS

59

## 4 AUTHORS, INCLUDING:



[Marian Wolszczak](#)

Lodz University of Technology

58 PUBLICATIONS 503 CITATIONS

SEE PROFILE

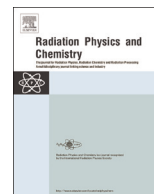


[Dorota Swiatla-Wojcik](#)

Lodz University of Technology

40 PUBLICATIONS 410 CITATIONS

SEE PROFILE



# Temperature dependence of the rate constant for hydrogen atom reaction with $\text{Cl}_2^\bullet$ in water by pulse radiolysis of aqueous HCl solution

L. Kazmierczak, J. Szala-Bilnik, M. Wolszczak, D. Swiatla-Wojcik\*

Institute of Applied Radiation Chemistry, Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland

## HIGHLIGHTS

- Rate constant  $k$  ( $\text{Cl}_2^\bullet + \text{H}$ ) has been determined over the range 25–75 °C.
- At 25 °C  $k$  ( $\text{Cl}_2^\bullet + \text{H}^\bullet$ ) =  $(6.1 \pm 0.6) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $E_a = 13.2 \pm 0.6 \text{ kJ/mol}$ .
- $E_a$  is lower than  $16.7 \text{ kJ mol}^{-1}$  expected for a diffusion-controlled reaction.
- The temperature dependence for  $k$  ( $\text{H}^\bullet + \text{Cl}_2$ ) in solution is provided.
- The room temperature value for  $k$  ( $\text{H}^\bullet + \text{H}_2\text{O}$ ) is critically evaluated.

## ARTICLE INFO

### Article history:

Received 22 April 2015

Received in revised form

9 June 2015

Accepted 14 July 2015

Available online 16 July 2015

### Keywords:

Pulse radiolysis

Dichloride anion ( $\text{Cl}_2^\bullet$ )

Hydrogen atom

Water

Chlorine

Rate constant

Activation energy

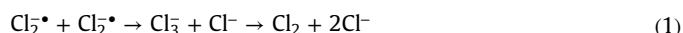
## ABSTRACT

The temperature dependence of the rate constant for the reaction of dichloride anion radical ( $\text{Cl}_2^\bullet$ ) with atomic hydrogen ( $\text{H}^\bullet$ ) in water up to 75 °C has been determined by pulse radiolysis of deaerated 0.1 M HCl solution. The room temperature value is  $(6.1 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The activation energy of  $(13.2 \pm 0.6) \text{ kJ mol}^{-1}$  is less than  $16.7 \text{ kJ mol}^{-1}$ , expected for the diffusion-controlled reaction. Based on the temperature dependence of the rate constant for the reactions  $\text{H}^\bullet + \text{Cl}_2^\bullet$  and  $\text{H}^\bullet + \text{Cl}_2$ , derived in this work, and on that reported earlier (Szala-Bilnik et al., 2014) for  $\text{Cl}_2^\bullet + \text{Cl}_2^\bullet$ , we show that a value of  $(10 \pm 2) \text{ M}^{-1} \text{ s}^{-1}$  determined by Hartig and Getoff (1982) for  $k$  ( $\text{H}^\bullet + \text{H}_2\text{O}$ ) in water at 25 °C is overestimated by at least two orders of magnitude.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

To assess the effect of chloride ion impurity on radiation-assisted hydrogen production or radiation enhanced stress-corrosion cracking in water-cooled nuclear power plants, data on the temperature dependence of rate constants for  $\text{Cl}_2^\bullet$  reactions with primary radical species are necessary because oxidation of chloride ions by  $\text{HO}^\bullet$  radicals in aqueous acidic solutions is known to produce the  $\text{Cl}_2^\bullet$  as an intermediate (Jayson et al., 1973). Rate constants for reactions involving  $\text{Cl}_2^\bullet$  are also of interest for modelling atmospheric halogen chemistry (Yu and Barker, 2003). Recently, we have reported (Szala-Bilnik et al., 2014) on the temperature dependence of the rate constant,  $k_1$ , for the disproportionation reaction (1)



The intermediate  $\text{Cl}_3$  ion has a very low stability constant,  $K_{\text{Cl}_3} = \frac{[\text{Cl}_3]}{[\text{Cl}_2][\text{Cl}^-]} = 0.18 \pm 0.02 \text{ M}^{-1}$  (on average) (Wang et al., 1994), and rapidly dissociates to produce chlorine. The overall rate constant  $k_1 = (7.35 \pm 0.53) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at 22 °C (at zero ionic strength) and the activation energy of  $10.89 \pm 0.37 \text{ kJ mol}^{-1}$ , over the temperature range 22–86 °C, were determined using pulse radiolysis of 0.1 M NaCl + 1 mM  $\text{HClO}_4$  aqueous solution (Szala-Bilnik et al., 2014). Since the temperature dependence of  $k_1$  was well reproduced by the Noyes equation assuming the activationless chemical step,  $6.50 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \text{ K}^{-1} \times T$ , it suggests that the rate of reaction (1) is similar to the recombination rate of two  $\text{HO}^\bullet$  radicals (Elliot et al., 1990).

This work has the aim of providing the temperature dependence of the rate constant,  $k_2$ , for reaction (2) of the hydrogen atom with  $\text{Cl}_2^\bullet$ .

\* Corresponding author.

E-mail address: [swiatlad@p.lodz.pl](mailto:swiatlad@p.lodz.pl) (D. Swiatla-Wojcik).



The room temperature values of  $k_2$ ,  $(7 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , measured by Navaratnam et al. (1980), and  $(8.0 \pm 1.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , reported by Lierse et al. (1987), are close to the value expected for a diffusion-controlled reaction. If, however, the behaviour of  $\text{Cl}_2^\bullet$  is similar to that of  $\text{HO}^\bullet$  and given that the reaction of  $\text{HO}^\bullet$  with  $\text{H}^\bullet$  is not a diffusion-controlled reaction at elevated temperatures (Buxton and Elliot, 1993), the same can be expected for  $k_2$ .

The kinetics of reaction (2) have been determined by measuring the decay of  $\text{Cl}_2^\bullet$  in an irradiated 0.1 M HCl solution saturated with  $\text{N}_2$ . In this system  $\text{H}^\bullet$  atoms are present in a concentration similar to that of  $\text{Cl}_2^\bullet$ . At high concentration of radicals the principal reactions are (1)–(3).

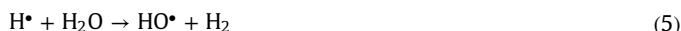


Since reaction (1) produces chlorine we also consider reaction (4).



In the HCl chemical laser, the reaction of  $\text{H}^\bullet$  with  $\text{Cl}_2$  is an important source of a vibrationally excited HCl molecule and atomic chlorine  $\text{Cl}^\bullet$ . In aqueous solution, at high  $\text{Cl}^-$  concentration, subsequent reaction of  $\text{Cl}^\bullet$  with  $\text{Cl}^-$  produces  $\text{Cl}_2^\bullet$ .

Measurements made for the same system but at lower dose, gave us the opportunity to critically evaluate the room temperature value of the rate constants for reaction (5) of atomic hydrogen  $\text{H}^\bullet$  with water.



A value of  $10 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$  first reported by Hartig and Getoff (1982) from a photolysis study of alkaline solutions was later questioned (Shiraishi et al., 1994; Swiatla-Wojcik and Buxton, 2005, 2010; Bartels, 2009) as being highly overestimated compared to thermodynamic estimations assuming equilibrium between the forward and backward steps. An additional aspect of our measurements is to provide upper limits for  $k_5$  over the temperature range 25–75 °C.

## 2. Experimental section

All experiments were carried out by pulse radiolysis coupled with optical detection at 340 nm, being the absorption maximum of  $\text{Cl}_2^\bullet$ . The aqueous solutions of 0.1 M HCl were deoxygenated by purging with high purity  $\text{N}_2$ . In this system only  $\text{Cl}_2^\bullet$  gives rise to the absorption at 340 nm (Jayson et al., 1973; Lierse et al., 1987). As described in our earlier publication (Szala-Bilnik et al., 2014) the optical path of the cell was 1 cm and the optical absorption was recorded using a monochromator ARC SpectraPro275, a photomultiplier R 928 Hamamatsu Photonics and an oscilloscope Tektronix TDS 540 MHz. We traced the decay of absorbance of  $\text{Cl}_2^\bullet$  over the temperature range 25–75 °C. At each temperature we recorded 3–7 independent traces. The  $\text{Cl}_2^\bullet$  molar absorption coefficient  $\epsilon_{340} = 9600 \text{ M}^{-1} \text{ cm}^{-1}$  (Adams et al., 1995) was assumed for all temperatures.

The kinetics of reaction (2) has been determined by measuring the decay of  $\text{Cl}_2^\bullet$  in 0.1 M HCl solution irradiated with a 17 ns pulse of high-energy electrons from 6 MeV ELU-6 linear accelerator. The dose per 17 ns pulse was in the range 55–60 Gy as measured at room temperature using  $\text{N}_2\text{O}$ -saturated 0.01 M solution of potassium thiocyanate (KSCN) as the dosimeter and taking  $G\epsilon_{475} = 5.28 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$  (Buxton and Stuart, 1995). The stock 0.1 M HCl solution used for these experiments was of the purest

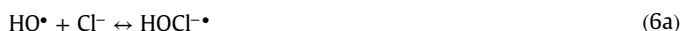
commercially available grade from Sigma-Aldrich.

Other experiments were conducted with a 7 ns pulse and a dose per pulse in the range 16–18 Gy. The stock 1 M HCl solution used for these experiments was of the purest commercially available grade from Sigma-Aldrich and was then diluted to 0.1 M using the Milipore water.

## 3. Results and discussion

### 3.1. Diffusion-kinetic modelling of deaerated 0.1 M HCl solution

Dichloride radical anion and atomic hydrogen are the main transient species produced by fast electron radiolysis of deaerated 0.1 M HCl aqueous solution. To find a relation between the radiation chemical yield of  $\text{Cl}_2^\bullet$ ,  $G(\text{Cl}_2^\bullet)$ , and the yield of  $\text{H}^\bullet$ ,  $G(\text{H}^\bullet)$ , diffusion-kinetic calculations have been performed using the modelling procedure described previously (Swiatla-Wojcik, 2008, 2009). Under the experimental conditions the hydrated electron is converted to  $\text{H}^\bullet$  by reaction with  $\text{H}_3\text{O}^+$  ions in less than 5 ns. Initially, the decay of the  $\text{HO}^\bullet$  radical in the spur is due to the self-reaction producing hydrogen peroxide. At longer times  $\text{HO}^\bullet$  is converted to  $\text{Cl}_2^\bullet$  by reactions (6a–c)



In 0.1 M HCl solution, equilibrium (6c) lies far to the right (Buxton et al., 1998), and the overall rate constant,  $k_6$ , for the conversion of  $\text{HO}^\bullet$  to  $\text{Cl}_2^\bullet$  depends on the ion concentration,  $c_{\text{H}^+}$ ,  $c_{\text{Cl}^-}$ , and the mean activation coefficient,  $\gamma_{\pm}$ , according to Eq. (7) (Jayson et al., 1973).

$$k_6 = k_{6a} k_{6b} c_{\text{H}^+} c_{\text{Cl}^-} \gamma_{\pm}^2 / (k_{-6a} + k_{6b} c_{\text{H}^+} \gamma_{\pm}) \quad (7)$$

Taking  $\gamma_{\pm} = 0.796$ ,  $k_{6a} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{-6a} = 6.1 \times 10^9 \text{ s}^{-1}$ ,  $k_{6b} = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (Jayson et al., 1973) we obtain a value of  $7.4 \times 10^7 \text{ s}^{-1}$  for  $k_6$  at room temperature. Given that the forward steps of reactions (6a)–(6c) are diffusion controlled and that the equilibria (6b) and (6c) lie to the right the overall effect of temperature on  $k_6$  depends on an activation energy  $E_{a(-6a)}$ , which is unknown. Assuming  $E_{a(-6a)} = 20 \text{ kJ mol}^{-1}$  the overall temperature dependence for  $k_6$  can be modelled using the Arrhenius dependence and a value of  $18 \text{ kJ mol}^{-1}$  for an activation energy. It should be noted that under our experimental conditions calculations are not sensitive to  $E_{a(-6a)}$ . Results obtained for  $E_{a(-6a)} \approx 40 \text{ kJ mol}^{-1}$ , which gives  $k_6$  almost independent of temperature, were much the same as those discussed below.

The G-values calculated for  $\text{Cl}_2^\bullet$  and  $\text{H}^\bullet$  at the end of the radiation chemical stage, when the spur chemistry is complete, are presented in Table 1.  $G(\text{Cl}_2^\bullet)$  recalculated according to the applied dose provides the expected initial concentration of  $\text{Cl}_2^\bullet$ ,  $c_{\text{Cl}_2^\bullet}^{\text{calc}}(0)$ . As can be seen  $c_{\text{Cl}_2^\bullet}^{\text{calc}}(0)$  compares well with  $c_{\text{Cl}_2^\bullet}^{\text{abs}}(0)$  measured at the absorption maximum.

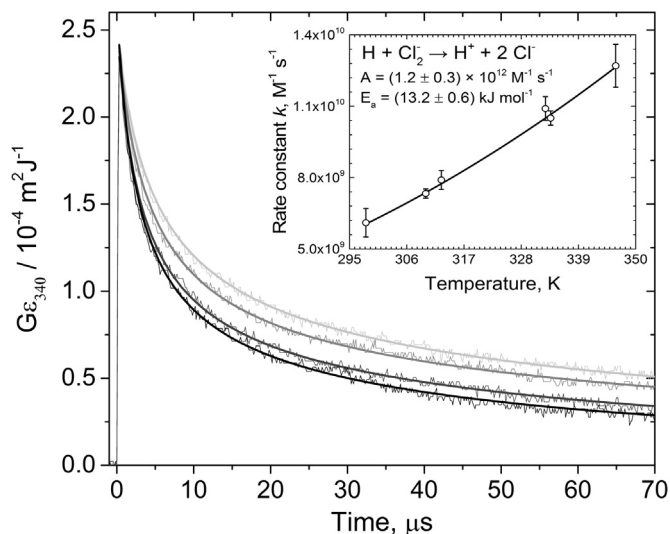
### 3.2. Reaction of atomic hydrogen with $\text{Cl}_2^\bullet$

Typical time profiles of the decay of  $\text{Cl}_2^\bullet$  recorded at 340 nm are displayed in Fig. 1. The signals were fitted using FACSIMILE 4 software, taking into account reactions (1)–(4), and allowing  $k_2$  to vary. The amount of hydrogen peroxide, formed prior the

**Table 1**

The G-values of  $\text{H}^\bullet$  and  $\text{Cl}_2^\bullet$  calculated for fast electron radiolysis of 0.1 M HCl using the spur modelling procedure for acidic solutions (Swiatla-Wojcik, 2008, 2009). The last two columns show the initial concentration of  $\text{Cl}_2^\bullet$ :  $c_{\text{Cl}_2^\bullet}^{\text{calc}}(0)$  – calculated using  $G(\text{Cl}_2^\bullet)$  and the dose value, and  $c_{\text{Cl}_2^\bullet}^{\text{abs}}(0)$  – obtained from the absorption maximum assuming  $\epsilon_{340} = 9600 \text{ M}^{-1} \text{ cm}^{-1}$ .

Temp. (°C)	$G(\text{H}^\bullet)$ ( $\mu\text{mol J}^{-1}$ )	$G(\text{Cl}_2^\bullet)$ ( $\mu\text{mol J}^{-1}$ )	$c_{\text{Cl}_2^\bullet}^{\text{calc}}(0)$ ( $\mu\text{M}$ )	$c_{\text{Cl}_2^\bullet}^{\text{abs}}(0)$ ( $\mu\text{M}$ )
25	0.38	0.33	$16.9 \pm 0.6$	$17.9 \pm 0.8$
40	0.39	0.35	$18.7 \pm 0.7$	$19.5 \pm 0.3$
60	0.39	0.37	$19.8 \pm 0.7$	$18.2 \pm 0.2$
80	0.40	0.39	$20.0 \pm 0.7$	$19.1 \pm 0.5$



**Fig. 1.** Transient absorption of  $\text{Cl}_2^\bullet$  in  $\text{N}_2$ -saturated aqueous 0.1 M HCl solution recorded at 340 nm after a 17 ns electron pulse. The profiles from top to bottom correspond to 25, 36.5, 60.5, and 73 °C. The solid line through each experimental trace is the FACSIMILE fit obtained taking into account reactions (1)–(4), and allowing  $k_2$  to vary as described in Section 3.2. Inset shows  $k_2$  as a function of temperature and a weighted Marquardt-Levenberg nonlinear fit to the Arrhenius equation.

scavenging of  $\text{HO}^\bullet$  by  $\text{Cl}^-$  ions,  $G(\text{H}_2\text{O}_2) = 6.2 \times 10^{-2} \mu\text{mol J}^{-1}$  at 25 °C, is too small to interfere with the decay kinetics of  $\text{Cl}_2^\bullet$ . In the fitting procedure the initial concentration of  $\text{Cl}_2^\bullet$  has been assumed to be  $c_{\text{Cl}_2^\bullet}^{\text{abs}}(0)$ , and the initial concentration of  $\text{H}^\bullet$ ,  $c_{\text{H}}(0)$ , has been determined from Eq. (8) interpolating the temperature dependence of the G-values obtained from the diffusion-kinetic modelling (see Table 1).

$$c_{\text{H}}(0) = c_{\text{Cl}_2^\bullet}^{\text{abs}}(0) \times \frac{G(\text{H}^\bullet)}{G(\text{Cl}_2^\bullet)} \quad (8)$$

The temperature dependence for  $k_3$  was taken from (Sehested and Christensen, 1990), and that for  $k_1$  from our earlier publication

(Szala-Bilnik et al., 2014). The values  $k_1^0$  at zero ionic strength,  $I=0$ , have been recalculated to  $I=0.1 \text{ M}$  by dividing  $k_1^0$  by  $\gamma_{\pm}^2$ . We should note here an overlooked mistake in Eq. (7) in Ref. (Szala-Bilnik et al., 2014). The value of the mean activation coefficient,  $\gamma_{\pm} = 0.796$  for 0.1 M HCl at 25 °C has been scaled with temperature as previously (Szala-Bilnik et al., 2014):

$$\log \gamma_{\pm(T)} = \log \gamma_{\pm(298)} \times \frac{A_{\gamma} \sqrt{I} / (1 + B_{\gamma} \sqrt{I})}{A_{298} \sqrt{I} / (1 + B_{298} \sqrt{I})} \quad (9)$$

where  $A_{\gamma} = 1.825 \cdot 10^6 \times (\epsilon \cdot T)^{-3/2}$ ,  $B_{\gamma} = 150.87 \times (\epsilon \cdot T)^{-1/2}$ ,  $T$  is absolute temperature,  $\epsilon$  is the dielectric constant of water, and  $A_{298}$ ,  $B_{298}$  denote  $A_{\gamma}$ ,  $B_{\gamma}$  coefficients calculated for 298 K. In Eq. (8) in Ref. (Szala-Bilnik et al., 2014) the symbol log was omitted by mistake.

The temperature dependence of  $k_4$  has been modelled using the Noyes relationship:

$$k_{\text{calc}}^{-1} = k_{\text{diff}}^{-1} + k_{\text{react}}^{-1} \quad (10)$$

where the reciprocal calculated value,  $k_{\text{calc}}$ , is represented by the sum of the reciprocal diffusion-controlled rate constant, given by the Smoluchowski Eq. (11) and the reciprocal rate constant of the chemical step, assumed to follow the Arrhenius dependence provided by Wagner et al. (1976) for the gaseous reactants (see Table 2 for details).

$$k_{\text{diff}} = 4\pi N_{\text{Av}} (D_1 + D_2) \times (R_1 + R_2) \quad (11)$$

In Eq. (11)  $N_{\text{Av}}$  is the Avogadro number,  $R_1$  and  $R_2$  are the reaction radii of the reactants, taken as independent of temperature, and  $D_1$ ,  $D_2$ , are the diffusion coefficients scaled with temperature. Values for  $D$ -coefficients at 25 °C and details of the scaling procedure are given in Table 2.

The rate constant for reaction (2) was fitted to reproduce the recorded decay profiles of  $\text{Cl}_2^\bullet$  at a given temperature. The FACSIMILE fits for  $k_2$  are listed in Table 3 along with the values assumed for  $k_4$ . The room temperature value,  $(6.1 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , obtained for  $k_2$  compares well with the literature data  $(7 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  multiplied by 0.917 and with  $(8.0 \pm 1.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  multiplied by 0.844 due to a difference in the extinction coefficient  $8800 \text{ M}^{-1} \text{ s}^{-1}$  assumed by Navaratnam et al. (1980) and  $8100 \text{ M}^{-1} \text{ s}^{-1}$  taken by Lierse et al. (1987), respectively. An inset in Fig. 1 shows a Marquardt-Levenberg nonlinear curve fit to the Arrhenius equation obtained using the OriginPro 2015 software. The respective values of the pre-exponential factor and the activation energy are  $A = (1.2 \pm 0.3) \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$  and  $E_a = (13.2 \pm 0.6) \text{ kJ mol}^{-1}$  ( $R^2 = 0.990$ ). The activation energy is lower than  $(16.7 \pm 0.1) \text{ kJ mol}^{-1}$  calculated for  $k_{\text{diff}}$  using the temperature dependence of the diffusion coefficients for  $\text{Cl}_2^\bullet$  and  $\text{H}^\bullet$  from Table 2. Therefore, we have used the Noyes relationship to describe the temperature dependence of  $k_2$  and matched the experimental points assuming  $k_{\text{react}} = A' T \exp[-E_a'/(RT)]$ , where  $A' = (1.2 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  and  $E_a' = (9.4 \pm 0.7) \text{ kJ mol}^{-1}$  (see Fig. 2).

**Table 2**

Parameters for modelling rate constants of reactions (2) and (4) using the Noyes relationship (Eq. (10)) over the temperature range 25–75 °C: reaction radii of the reactants,  $R_1$ ,  $R_2$ , diffusion coefficients at 25 °C,  $D_{1(25)}$ ,  $D_{2(25)}$ , the temperature dependence of the rate of the chemical step,  $k_{\text{react}}$ .

Reaction	$R_1$ (nm)	$R_2$ (nm)	$D_{1(25)}$ ( $\text{m}^2 \text{ s}^{-1}$ )	$D_{2(25)}$ ( $\text{m}^2 \text{ s}^{-1}$ )	$k_{\text{react}}$ ( $\text{M}^{-1} \text{ s}^{-1}$ )
(1) $\text{Cl}_2^\bullet + \text{Cl}_2^\bullet$	0.185	0.185	$1.41 \times 10^{-9a}$	$1.41 \times 10^{-9a}$	$6.5 \times 10^6 \times T[\text{K}]$
(2) $\text{H}^\bullet + \text{Cl}_2^\bullet$	0.19	0.185	$7 \times 10^{-9b}$	$1.41 \times 10^{-9a}$	$1.2 \times 10^9 \times T \times \exp(-1130/T[\text{K}])$
(4) $\text{H}^\bullet + \text{Cl}_2$	0.19	0.185	$7 \times 10^{-9b}$	$1.38 \times 10^{-9a}$	$8.7 \times 10^{10} \times \exp(-601/T[\text{K}])$

The diffusion coefficients have been scaled with increasing temperature using:

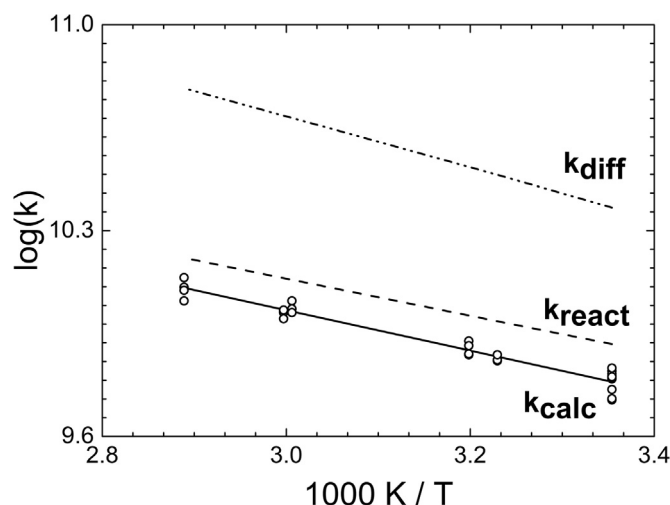
<sup>a</sup>  $D_T/D_{25} = T[\text{K}]/\eta_T^W/(298/\eta_{25}^W)$  and the viscosity of water,  $\eta_T^W$ , (Sengers and Watson, 1986).

<sup>b</sup>  $D_T = D_{25} \times D_1^W/D_{25}^W$  (Elliot et al., 1990) and the temperature dependence of the self-diffusion coefficient of water,  $D_1^W$ , (Krynicky et al., 1978).

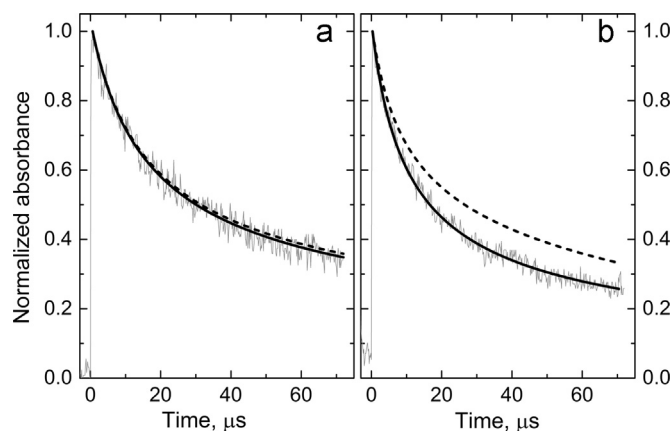
**Table 3**  
Rate constants for reactions (2) and (4) for selected temperatures from the range 25–75 °C.<sup>a</sup>

Temperature (°C)	$k_2 \times 10^{-9} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$	$k_4 \times 10^{-9} \text{ (M}^{-1} \text{ s}^{-1}\text{)}$
25.0 ± 0.1	6.1 ± 0.6	9.4 ± 0.4
36.5 ± 0.1	7.3 ± 0.2	11.3 ± 0.2
60.5 ± 0.5	10.5 ± 0.3	12.5 ± 0.7
73.0 ± 1.0	12.7 ± 0.9	13.8 ± 0.5

<sup>a</sup> Errors are ± 1 S.D.



**Fig. 2.** Temperature dependence of the rate constant for reaction (2) calculated from the Noyes relationship (Eq. (10)) using the parameters given in Table 2. Also shown are  $k_{\text{diff}}$  and  $k_{\text{react}}$ .



**Fig. 3.** Oscilloscope traces normalized to the maximum transient absorption of  $\text{Cl}_2^{\bullet-}$  in  $\text{N}_2$ -saturated aqueous 0.1 M HCl solution recorded at 340 nm after a 7 ns electron pulse: 25 °C (left) and 60.5 °C (right) and the FACSIMILE decay profiles calculated assuming the reaction set (1–4) (solid lines) and (1–6(a–c)) (dashed lines) (see Section 3.3 for details).

### 3.3. Reaction of atomic hydrogen with water

Measurements of transient absorption of  $\text{Cl}_2^{\bullet-}$  in  $\text{N}_2$ -saturated aqueous 0.1 M HCl solution have been made for the same system but at low dose (16–18 Gy) to reduce a contribution from radical-radical reactions. Fig. 3 shows normalized oscilloscope traces recorded at room temperature (left panel) and at 60.5 °C (right panel). These traces are compared with FACSIMILE decay profiles simulated for the reaction set (1–4) (solid lines) and (1–6(a–c)) (dashed lines). In the latter simulation the decay of  $\text{H}^{\bullet}$  atom in reaction with water competes with reactions (2–4) and the  $\text{HO}^{\bullet}$

radical generated in reaction (5) is converted to  $\text{Cl}_2^{\bullet-}$  by reactions (6a–c). At low dose a slower decay of  $\text{Cl}_2^{\bullet-}$  should be seen on the scale time of our experiment when a fraction of  $\text{Cl}_2^{\bullet-}$  reacted with  $\text{H}^{\bullet}$  is reduced by reaction (5). Hartig and Getoff (1982) value of  $10 \text{ M}^{-1} \text{ s}^{-1}$  (or  $5.5 \times 10^2 \text{ s}^{-1}$ ) assigned to  $k_5$  at 25 °C results in a slightly slower decay, but both simulated lines reproduce the experimental profile shown in the left panel in Fig. 3. However, taking an activation energy  $E_a = 75 \text{ kJ mol}^{-1}$ , which corresponds to reaction (5) in the gas phase (Baulch et al., 2005), one obtains  $2.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  (or  $1.4 \times 10^4 \text{ s}^{-1}$ ) for  $k_5$  at 60.5 °C. This value is high enough to provide a critical test for the data reported by Hartig and Getoff (1982). As can be seen in the right panel in Fig. 3 the experimental profile is well reproduced by the solid line, but the dashed line shows a significant mismatch. To eliminate this mismatch we had to decrease  $k_5$  to  $1.5 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$  (or  $8.0 \times 10^2 \text{ s}^{-1}$ ). Assuming again  $E_a = 75 \text{ kJ mol}^{-1}$  the obtained threshold leads to a value for  $k_5$  of  $5.9 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. Since an activation energy for reaction (5) in aqueous solution can be higher than in the gas phase due to hydrogen bonding of  $\text{H}_2\text{O}$ , this result shows that the value reported by Hartig and Getoff (1982) is overestimated by at least two orders of magnitude. At the same time one can evaluate the thermodynamic estimate  $k_5 \approx 1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C (Shiraishi et al., 1994; Swiatla-Wojcik and Buxton 2010; Bartels, 2009). Assuming  $E_a$  even as high as  $100 \text{ kJ mol}^{-1}$ , one obtains a value of  $4 \times 10^{-1} \text{ s}^{-1}$  for  $k_5$  at 60.5 °C, which is much below the obtained threshold  $8 \times 10^2 \text{ s}^{-1}$ .

In conclusion, based on pulse radiolysis measurements of  $\text{Cl}_2^{\bullet-}$  decay in 0.1 M HCl aqueous solution at elevated temperature we have showed that the room temperature rate constant for the  $\text{H}^{\bullet}$  atom reaction with water should be of the order of  $1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  or lower. This result does not rule out the thermodynamic estimate for  $k_5$  of ca.  $1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C.

### Acknowledgement

Financial support under Research task no. 7 “Study of hydrogen generation processes in nuclear reactors under regular operation conditions and in emergency cases, with suggested actions aimed at upgrade of nuclear safety” financed by the National Research and Development Centre in the framework of the strategic research project entitled “Technologies Supporting Development of Safe Nuclear Power Engineering” is greatly acknowledged.

The authors thank Dr G. V. Buxton for suggestions on the experimental system and helpful discussion.

### References

- Adams, D.J., Barlow, S., Buxton, G.V., Malone, T.N., Salmon, G.A., 1995. Evaluation of the stability constant of  $\text{Cl}_2^{\bullet-}$  in neutral aqueous solution. *J. Chem. Soc. Faraday Trans. 91*, 3303–3305.
- Bartels, D.M., 2009. Comment on the possible role of the reaction  $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$  in the radiolysis of water at high temperatures. *Radiat. Phys. Chem.* 78, 191–194.
- Baulch, D.L., Bowman, C.T., Cobos, C.J., Cox, R.A., Just, Th, Kerr, J.A., Philling, M.J., Stocker, D., Troe, J., Tsang, W., Walker, R.W., Warnatz, J., 2005. Evaluated kinetic data for combustion modelling: supplement II. *J. Phys. Chem. Ref. Data* 34, 757–1397.
- Buxton, G.V., Elliot, A.J., 1993. Temperature dependence of the rate constant for the reaction  $\text{H} + \text{OH}$  in liquid water up to 200 °C. *J. Chem. Soc. Faraday Trans. 89*, 485–488.
- Buxton, G.V., Bydder, M., Salmon, G.A., 1998. Reactivity of chlorine atoms in aqueous solution. Part 1. The equilibrium  $\text{Cl}^{\bullet} + \text{Cl}^- = \text{Cl}_2^{\bullet-}$ . *J. Chem. Soc. Faraday Trans. 94*, 653–657.
- Buxton, G.V., Stuart, C.R., 1995. Re-evaluation of the thiocyanate dosimeter for pulse radiolysis. *J. Chem. Soc. Faraday Trans. 91*, 279–281.
- Elliot, A.J., McCracken, D.R., Buxton, G.V., Wood, N.D., 1990. Estimation of rate constants for near-diffusion-controlled reactions in water at high temperatures. *J. Chem. Soc. Faraday Trans. 86*, 1539–1547.
- Hartig, K.J., Getoff, N., 1982. Reactivity of hydrogen atoms with liquid water. *J.*



- Photochem. 18, 29–38.
- Jayson, G.G., Parsons, B.J., Swallow, A.J., 1973. Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. *J. Chem. Soc. Faraday Trans. 1* 69, 1593–1607.
- Krynicky, K., Green, Ch. D., Sawyer, D.W., 1978. Pressure and temperature dependence of self-diffusion in water. *Faraday Discuss. Chem. Soc.* 66, 199–208.
- Lierse, Ch, Sullivan, J.C., Schmidt, K.H., 1987. Rates of oxidation of selected actinides by  $\text{Cl}_2$ . *Inorg. Chem.* 26, 1408–1410.
- Navaratnam, S., Parsons, B.J., Swallow, A.J., 1980. Some reactions of the dichloride anion radical. *Radiat. Phys. Chem.* 15, 159–161.
- Sehested, K., Christensen, H., 1990. The rate constant of bimolecular reaction of hydrogen atoms at elevated temperatures. *Radiat. Phys. Chem.* 36, 499–500.
- Sengers, J.V., Watson, J.T.R., 1986. Improved international formulations for the viscosity and thermal conductivity of water substance. *J. Phys. Chem. Ref. Data* 15, 1291–1315.
- Shiraishi, H., Sunaryo, G.R., Ishigure, K., 1994. Temperature dependence of equilibrium and rate constants of reactions inducing conversion between hydrated electron and atomic hydrogen. *J. Phys. Chem.* 98, 5164–5173.
- Swiatla-Wojcik, D., Buxton, G.V., 2005. On the possible role of the reaction  $\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}$  in the radiolysis of water at high temperatures. *Radiat. Phys. Chem.* 74 (3–4), 210–219.
- Swiatla-Wojcik, D., 2008. Computation of the effect of pH on spur chemistry in water radiolysis at elevated temperatures. *Nukleonika* 53, S31–S37.
- Swiatla-Wojcik, D., 2009. Modelling spur chemistry for alkaline and acidic water at high temperatures. *Res. Chem. Intermed.* 35, 519–530.
- Swiatla-Wojcik, D., Buxton, G.V., 2010. Reply to comment on the possible role of the reaction  $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$  in the radiolysis of water at high temperatures. *Radiat. Phys. Chem.* 79, 52–56.
- Szala-Bilnik, J., Pierscieniewska, P., Wolszczak, M., Swiatla-Wojcik, D., 2014. Temperature dependence of the rate constant for the bimolecular recombination of  $\text{Cl}_2$  in water – a pulse radiolysis study. *Radiat. Phys. Chem.* 97, 184–187.
- Wang, T.X., Kelley, M.D., Cooper, J.N., Beckwith, R.C., Margerum, D.W., 1994. Equilibrium, kinetic, and UV-spectral characteristics of aqueous bromine chloride, bromine, and chlorine species. *Inorg. Chem.* 33, 5872–5878.
- Wagner, H. Gg, Welzbacher, U., Zellner, R., 1976. Rate measurements for the reaction  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$  by Lyman- $\alpha$  fluorescence. *Ber. Bunsenges. Phys. Chem.* 80, 902–908.
- Yu, X.-Y., Barker, J.R., 2003. Hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions. I. chemical mechanism. *J. Phys. Chem. A* 107, 1313–1324.