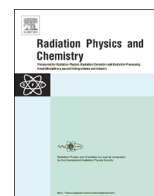




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Short communication

Rate of reaction of the hydrogen atom with nitrous oxide in ambient water

Lukasz Kazmierczak, Dorota Swiatla-Wojcik*, Joanna Szala-Bilnik, Marian Wolszczak

Institute of Applied Radiation Chemistry, Faculty of Chemistry, Technical University of Lodz, Zeromskiego 116, 90–924 Lodz, Poland

H I G H L I G H T S

- Rate of reaction $\text{H}^* + \text{N}_2\text{O} = \text{OH}^* + \text{N}_2$ in solution was measured by pulse radiolysis.
- N_2O -saturated 0.1 M HCl aqueous solution has been used.
- The reaction rate constant is $(9 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at $(24 \pm 1 \text{ }^\circ\text{C})$.

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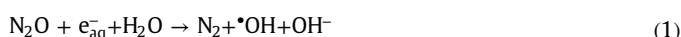
A B S T R A C T

The reaction of the hydrogen atom with nitrous oxide has been investigated by pulse radiolysis of N_2O -saturated 0.1 M HCl solution at room temperature ($24 \pm 1 \text{ }^\circ\text{C}$). The value of $(9 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ obtained for the reaction rate constant is between the early estimates $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ by Czapski and Jortner (1960) and $4.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ by Thomas (1969), and is much lower than $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ used recently (Janik et al., 2007; Ismail et al., 2013; Liu et al., 2015; Meesungnoen et al., 2015).

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1. Introduction

The reaction of the hydrogen atom with N_2O is of great importance in combustion chemistry (Miller and Bowman, 1989), in the reduction of nitrogen oxides to molecular nitrogen *via* reaction with ammonia (Miller et al., 1981), and in the degradation of pollutants, chlorpyrifos (Ismail et al., 2013), 4-chloroaniline (Sanchez et al., 2002), primidone (Liu et al., 2015), in N_2O -saturated water solutions. Since reaction (1) with the hydrated electron (e_{aq}^-) and reaction (2) with the H atom produce the hydroxyl radical (OH^*), the reduction potential of N_2O is also used in the oxidation of pollutants induced by electron beams (Emmi and Takács, 2008).



The rate of reaction (2) in the gas phase has been established over the range 350–2500 K using flame study, static systems,

discharge flow study, reflected shock waves, and shock-tube techniques (Baulch et al., 2005). Marshall et al. (1987) showed that below 800 K the exothermic reaction (2) is the main channel, since the branching ratio for two endothermic pathways, (3) and (4), is less than 10^{-4} .



Extrapolation of the temperature dependence for k_2 to 298 K gives the gas phase value of $6.16 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in agreement with $k_{2(\text{gas})} = 8.56 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ obtained for ambient conditions from the analytical formula provided by Diau and Lin (1995). The first rough estimate of $k_{2(\text{liq})} \sim 10^3 - 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in ambient aqueous solution was given by Czapski and Jortner (1960), who based it on the observation that k_2 is about 60 times smaller than the rate constant of the oxidation of ferrous ion by atomic hydrogen. Later, Thomas (1969) provided $k_{2(\text{liq})} = 4.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, although based on the observation by Czapski and Jortner (1960) and using $k(\text{H} + \text{Fe}^{2+}) = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Schwarz, 1963) one obtains $k_{2(\text{liq})} = 3.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Czapski and Peled (1968) measurements in

* Corresponding author.

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

alkaline N₂O-saturated solutions resulted in three estimates $(0.48 \pm 0.8) \times 10^6$, $(1.8 \pm 6.0) \times 10^6$, $(1.3 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, depending on the method. Since the first two estimates were very uncertain, Czapski and Peled accepted the value of $(1.3 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, showing good agreement with $k_{2(\text{liq})} \sim 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ obtained by Dainton and Walker (1965) but being higher than the earlier estimates by one or two orders of magnitude. The value $k_{2(\text{liq})} = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ has been recently used by many authors (Janik et al., 2007; Ismail et al., 2013; Liu et al., 2015; Meesungnoen et al., 2015). Although Janik et al. (2007) referred to the measurements by Czapski and Bielski (1993), we have found no information on reaction (2) in the referenced paper.

The aim of this work is to provide a critical test of the very divergent data on $k_{2(\text{liq})}$ by using pulse radiolysis measurements for N₂O-saturated 0.1 M HCl aqueous solution. In this system the $\bullet\text{OH}$ formed in reaction (2) is quickly converted to $\text{Cl}_2^{\bullet-}$ since $k_5 = 7.4 \times 10^7 \text{ s}^{-1}$ for 0.1 M HCl radical solution (Kazmierczak et al., 2015). As discussed in our previous paper (Kazmierczak et al., 2015), the decay rate of $\text{Cl}_2^{\bullet-}$ in 0.1 M HCl solution depends on the kinetics of reactions (6)–(9).



In the N₂O-saturated system reaction (2) is expected to compete with reactions (7)–(9).

2. Experimental section

Electron pulse radiolysis experiments were carried out using 7 ns and 17 ns pulses from 6 MeV ELU-6 linear accelerator, coupled with optical detection at 340 nm. The dose was (14.0 ± 0.4) Gy per 7 ns pulse and (46.5 ± 1.4) Gy per 17 ns pulse, as evaluated using N₂O-saturated 0.01 M solution of potassium thiocyanate (KSCN) as the dosimeter and taking $G_{\text{E}_{475}} = 5.28 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ (Buxton and Stuart, 1995). The stock 0.1 M HCl solution was of the purest commercially available grade from Sigma-Aldrich. The solutions were deoxygenated by purging with high purity N₂O. According to the Henry's constant, $0.0247 \text{ M atm}^{-1}$ at 25 °C (Ma'mun and Svendsen, 2009), the concentration of N₂O in the saturated solution was 24.7 mM. We traced the decay of transient absorption of $\text{Cl}_2^{\bullet-}$ at room temperature (24 ± 1) °C. The optical path of the cell was 1 cm. Ten independent traces were recorded for each pulse. The molar absorption coefficient $\epsilon_{340} = 9600 \text{ M}^{-1} \text{ cm}^{-1}$ (Adams et al., 1995) was assumed to convert the recorded absorbance to the molar concentration. The time-dependent concentration profiles were fitted using FACSIMILE 4 software.

3. Results and discussion

Fig. 1 presents a comparison of the normalized absorption traces of $\text{Cl}_2^{\bullet-}$ in N₂O-saturated 0.1 M HCl solution with the profiles recorded for N₂-saturated solution (Kazmierczak et al., 2015). The decay of $\text{Cl}_2^{\bullet-}$ in N₂O-saturated solution is slower, indicating a significant contribution of reaction (2).

To establish the value of k_2 the unnormalized concentration

profiles have been fitted taking the rate constants from Table 1 and allowing k_2 to vary. Although $\text{Cl}_2^{\bullet-}$ and H^{\bullet} are the main transient species produced by fast electron radiolysis of deaerated 0.1 M HCl aqueous solution, some amount of hydrogen peroxide is formed in radiation spurs prior to the scavenging of $\bullet\text{OH}$ by Cl^- ions. To find a relation between the primary radiation chemical yields of the reactants diffusion-kinetic calculations have been performed using the modelling procedure described previously (Swiatla-Wojcik, 2008, 2009; Kazmierczak et al., 2015). The primary yields, $G(\text{Cl}_2^{\bullet-}) = 0.40 \mu\text{mol J}^{-1}$, $G(\text{H}^{\bullet}) = 0.33 \mu\text{mol J}^{-1}$, $G(\text{H}_2\text{O}_2) = 0.06 \mu\text{mol J}^{-1}$, have been obtained assuming 10^{-7} s for the upper integration limit of the diffusion-kinetic differential equations describing the non-homogenous spur chemistry. We have found that the amount of H_2O_2 is too small to contribute to the decay of $\text{Cl}_2^{\bullet-}$. The calculated primary yields $G(\text{Cl}_2^{\bullet-})$ and $G(\text{H}^{\bullet})$ have been used to establish the initial concentration of H^{\bullet} , $c_{\text{H}^{\bullet}}^0$, from the following formula:

$$c_{\text{H}^{\bullet}}^0 = c_{\text{Cl}_2^{\bullet-}}^{\text{obs}} \times \frac{G(\text{H}^{\bullet})}{G(\text{Cl}_2^{\bullet-})} \quad (10)$$

where $c_{\text{Cl}_2^{\bullet-}}^{\text{obs}}$ is the initial concentration of $\text{Cl}_2^{\bullet-}$ obtained from the absorption maximum, assuming $\epsilon_{340} = 9600 \text{ M}^{-1} \text{ cm}^{-1}$. The mean of $c_{\text{Cl}_2^{\bullet-}}^{\text{obs}}$ obtained in 7 and 17 ns measurements, 5.3 ± 0.2 and $17.7 \pm 0.7 \text{ M}$, respectively, shows good agreement with 5.5 ± 0.2 and $18.3 \pm 0.6 \text{ M}$ calculated from $G(\text{Cl}_2^{\bullet-})$, and the respective dose

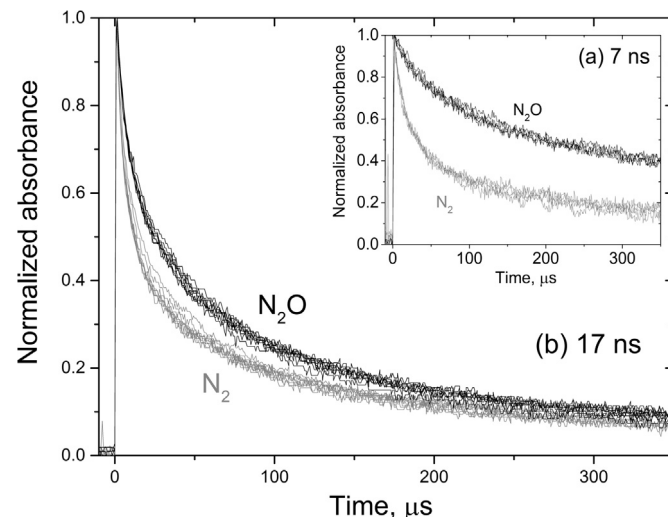


Fig. 1. The normalized-to-maximum transient absorbance of $\text{Cl}_2^{\bullet-}$ in pulse irradiated aqueous 0.1 M HCl solution saturated with N₂ (grey) and N₂O (black) recorded at 340 nm after (a) 7 ns and (b) 17 ns pulse. Data for the N₂-saturated system are from our previous paper (Kazmierczak et al., 2015).

Table 1

The room temperature rate constants of reactions assumed in the fitting procedure.

Rate constant, k	References and notes
$k_2 = (9 \pm 2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ $k_5 = 7.4 \times 10^7 \text{ s}^{-1}$	Fitted (this work) Calculated from Eq.(7) in Kazmierczak et al. (2015)
$k_6 = (1.27 \pm 0.13) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	The value $k_6^0 = (7.35 \pm 0.53) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 22 °C and zero ionic strength, $I=0$ Szala-Bilnik et al. (2014) recalculated for 25 °C and $I=0.1 \text{ M}$.
$k_7 = (6.1 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $k_8 = (7.6 \pm 1.9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $k_9 = 5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Kazmierczak et al. (2015) Kazmierczak et al. (2015) Sehested and Christensen (1990)

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