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**Experimental Determination of the Rate Constants of the  
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# Experimental Determination of the Rate Constants of the Reactions of $\text{HO}_2 + \text{DO}_2$ and $\text{DO}_2 + \text{DO}_2$

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## Abstract

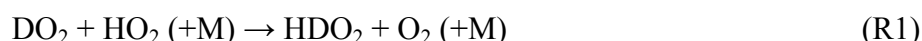
The rate constants of the reactions of  $\text{DO}_2 + \text{HO}_2$  (R1) and  $\text{DO}_2 + \text{DO}_2$  (R2) have been determined by the simultaneous, selective and quantitative measurement of  $\text{HO}_2$  and  $\text{DO}_2$  by cw-CRDS in the near infrared, coupled to a radical generation by laser photolysis.  $\text{HO}_2$  was generated by photolysing  $\text{Cl}_2$  in the presence of  $\text{CH}_3\text{OH}$  and  $\text{O}_2$ . Low concentrations of  $\text{DO}_2$  were generated simultaneously by adding low concentrations of  $\text{D}_2\text{O}$  to the reaction mixture, leading through isotopic exchange on tubing and reactor walls to formation of low concentrations of  $\text{CH}_3\text{OD}$  and thus formation of  $\text{DO}_2$ . Excess  $\text{DO}_2$  was generated by photolysing  $\text{Cl}_2$  in the presence of  $\text{CD}_3\text{OD}$  and  $\text{O}_2$ , small concentrations of  $\text{HO}_2$  were always generated simultaneously by isotopic exchange between  $\text{CD}_3\text{OD}$  and residual  $\text{H}_2\text{O}$ . The rate constant  $k_1$  at 295 K was found to be pressure independent in the range 25 – 200 Torr helium, but increased with increasing  $\text{D}_2\text{O}$  concentration  $k_1 = (1.67 \pm 0.03) \times 10^{-12} \times (1 + (8.2 \pm 1.6) \times 10^{-18} \text{ cm}^3 \times [\text{D}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$ . The rate constant for the  $\text{DO}_2$  self reaction  $k_2$  has been measured under excess  $\text{DO}_2$  concentration, and the  $\text{DO}_2$  concentration has been determined by fitting the  $\text{HO}_2$  decays, now governed by their reaction with  $\text{DO}_2$ , to the rate constant  $k_1$ . A rate constant with insignificant pressure dependence was found:  $k_2 = (4.1 \pm 0.6) \times 10^{-13} (1 + (2 \pm 2) \times 10^{-20} \text{ cm}^3 \times [\text{He}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$  as well as an increase of  $k_2$  with increasing  $\text{D}_2\text{O}$  concentration was observed:  $k_2 = (4.14 \pm 0.02) \times 10^{-13} \times (1 + (6.5 \pm 1.3) \times 10^{-18} \text{ cm}^3 \times [\text{D}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$ . The result for  $k_2$  is in excellent agreement with literature values, while this is the first determination of  $k_1$ .

## Introduction

The hydroperoxy radical,  $\text{HO}_2$ , is a major radical in oxidation chemistry. In the atmosphere its concentration is closely linked to the OH radical by recycling it through reaction with NO. The self reaction of  $\text{HO}_2$  radicals (R3) is a major sink for odd hydrogen in the atmosphere, and presents also the major source of  $\text{H}_2\text{O}_2$  in the stratosphere. The reaction has attracted a large interest in the last decades and its rate constant presents interesting features such as negative temperature dependence and pressure dependence. Small amounts of water vapor or methanol enhance the rate constant, while addition of  $\text{NH}_3$  initially enhances the rate constant but then slows down the reaction at higher concentrations [1,2,3,4,5,6,7,8,9,10,11]. An extended review on the current knowledge and on the interpretation of this behavior is given by Stone and Rowley [7].

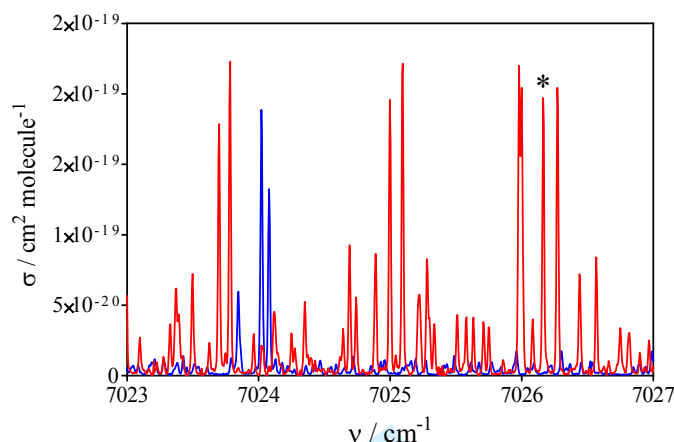
The self reaction of  $\text{DO}_2$ ,  $k_2$ , shows a similar behavior, but with a rate constant around four times slower than  $k_3$  and the pressure dependence roughly a factor of 2 weaker. The less pronounced pressure dependence for  $\text{DO}_2$  compared to  $\text{HO}_2$  is attributed to the faster approach to the high pressure limit for  $\text{DO}_2$  while the strong kinetic isotope effect has been explained in an early work by Mozurkewich and Benson [4] by using a cyclic transition state instead of the tetraoxide transition state favored by Patrick, Barker and Golden [12]. The six-membered ring complex as transition state has also been confirmed by more recent high level calculations [13],[14].

The rate constant of the cross reaction between the two isotopes  $\text{HO}_2$  and  $\text{DO}_2$



has never been measured to our knowledge. While this reaction is of no importance in the atmosphere, it might play a role in laboratory experiments, when deuterated compounds are used to elucidate reaction mechanisms [15]. The difficulty in measuring this rate constant is that both isomeric radicals need to be detected in a selective way. In most of the earlier works,  $\text{HO}_2$  or  $\text{DO}_2$  radicals have been detected by UV-absorption spectroscopy which does not allow a separation between both isomers, because their absorption spectra in the UV range are broad and unstructured. Thrush and Tyndall have in 1982 detected the  $\text{HO}_2$  radical selectively in the  $\nu_3$  band at  $1117 \text{ cm}^{-1}$  and have measured the rate constant of the self reaction [16]. Six years later, Martin and Thrush have in 1988 selectively detected the  $\text{DO}_2$  radical in the  $\nu_2$  band at  $1020 \text{ cm}^{-1}$  and measured the rate constant of the  $\text{DO}_2$  self reaction [17]. However, to our knowledge, no paper has reported so far experiments on the simultaneous, time resolved and selective detection of both isotopes. In the current work, we have used the selective detection of both radicals in the near IR range, where two highly structured absorption ranges can be found: the  $2\nu_1$  transition for  $\text{HO}_2$  lies at around  $6600 \text{ cm}^{-1}$  and has been extensively studied and used for its detection [10],[18],[19],[20],[21],[22],[23],[24],[25],[26]. This transition is also used in this work for the quantification of  $\text{HO}_2$ . The corresponding  $\text{DO}_2$  transition is expected to be around  $5000 \text{ cm}^{-1}$  [27], but has not been studied to our knowledge, probably due to increased experimental difficulties occurring in this wavelength range compared to  $6600 \text{ cm}^{-1}$ . Instead, the low-lying electronic transition of the  $\tilde{A}^2A' \leftarrow \tilde{X}^2A''$  000-000 band at around  $7000 \text{ cm}^{-1}$  has been studied and used for the detection of  $\text{DO}_2$  [15],[28],[29]. Being an electronic transition, the  $\text{HO}_2$  radical can be detected in the same wavelength range [29],[30],[31]. **Figure 1** presents a portion of the  $\tilde{A}^2A' \leftarrow \tilde{X}^2A''$  000-000 spectrum for  $\text{HO}_2$  (blue) and  $\text{DO}_2$  (red). The transition used in this work for quantifying the  $\text{DO}_2$  concentration

has been chosen to be free of interference from HO<sub>2</sub> transitions and is marked with an asterisk.



**Figure 1:** Portion of the HO<sub>2</sub> (blue) and DO<sub>2</sub> (red) spectrum at 25 Torr, adapted from [29]. The line marked with an asterisk indicates the line used in this work for DO<sub>2</sub> quantification.

In this work we present the experimental determination of  $k_1$ , by simultaneous selective detection of both isotopes. The rate constant of the self reaction of DO<sub>2</sub> radicals:



has also been measured. Both rate constant determinations are based on the determination of the absolute HO<sub>2</sub> concentration by fitting HO<sub>2</sub> decays to the well-known rate constant of the HO<sub>2</sub> self reaction, (R3):



In other words, the rate constants  $k_1$  and  $k_2$  have been measured relative to  $k_3$ .

## Experimental Section

Experiments have been carried out using pulsed laser photolysis coupled to cw-CRDS. The set-up has been described in detail elsewhere [29,[32],[33],[34]] and only a brief description will be given here. The experimental set-up contains two cw-CRDS paths, which cross the photolysis beam symmetrically in a small angle. This allows the simultaneous, time resolved and absolute detection of two species. An overlap between photolysis and detection beam of 37.7cm is obtained. To control if the photolysis laser is well aligned, *i.e.* both cw-CRDS paths sample the same path lengths, HO<sub>2</sub> radicals are detected in an initial experiment on both paths: the retrieved concentrations from both paths agreed to better than 5%.

Experiments have been carried out under either excess HO<sub>2</sub> over DO<sub>2</sub>, or excess DO<sub>2</sub> over HO<sub>2</sub>. HO<sub>2</sub> was detected on one path for all experiments within the 2ν<sub>1</sub> vibrational overtone

band at either the strongest transition at 6638.205 cm<sup>-1</sup> or, when HO<sub>2</sub> concentrations were high and absorption became too strong, on a smaller transition at 6638.58 cm<sup>-1</sup>. DO<sub>2</sub> has been detected on the other path in the  $\tilde{A}^2A' \leftarrow \tilde{X}^2A''$  000-000 band at 7026.16 cm<sup>-1</sup>.

The reaction is initiated by 351 nm excimer laser photolysis (Lambda Physik, LPX 202i) of Cl<sub>2</sub>



The laser fluence was typically 30-40 mJ cm<sup>-2</sup>, leading to a photolysis yield of around 1% for Cl<sub>2</sub>. HO<sub>2</sub> radicals were generated by the reaction of the Cl-atoms with CH<sub>3</sub>OH in the presence of O<sub>2</sub>:



For experiments with excess HO<sub>2</sub> over DO<sub>2</sub>, low concentrations of DO<sub>2</sub> radicals in the presence of excess HO<sub>2</sub> were generated by adding low concentrations of D<sub>2</sub>O to the gas flow. This way, rapid H/D isotope exchange between the labile -OH in CH<sub>3</sub>OH and D<sub>2</sub>O lead to formation of some CH<sub>3</sub>OD which then reacts with Cl [29]:



with subsequent formation of DO<sub>2</sub> through



Excess DO<sub>2</sub> over HO<sub>2</sub> was generated through the reaction of Cl atoms with CD<sub>3</sub>OD in the presence of O<sub>2</sub>:



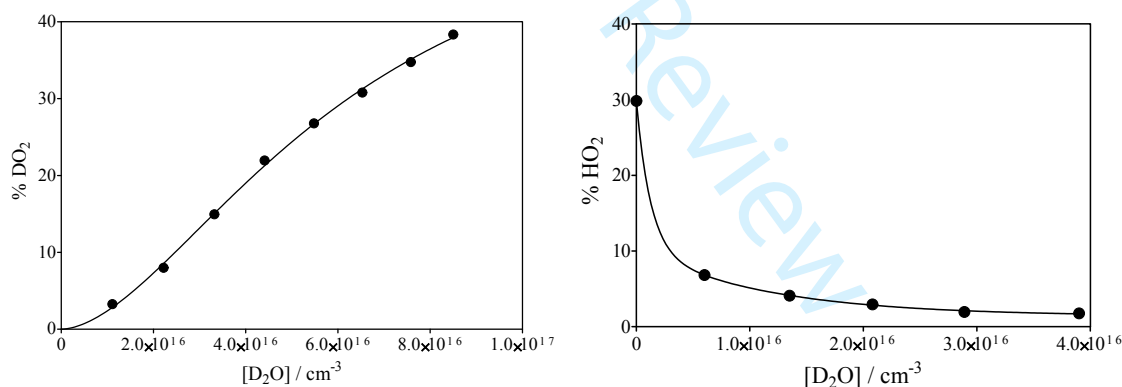
H<sub>2</sub>O, always present in the system, led through H/D exchange always to the formation of some CD<sub>3</sub>OH and subsequently to formation of HO<sub>2</sub> through:



In order to decrease the fraction of CD<sub>3</sub>OH and thus HO<sub>2</sub>, the gas flow was partially saturated with D<sub>2</sub>O by flowing a varying fraction of the bath gas Helium through a trap containing liquid D<sub>2</sub>O. Concentrations of CH<sub>3</sub>OH, CD<sub>3</sub>OD and D<sub>2</sub>O were estimated from partial pressures and flow rates, no information on the CD<sub>3</sub>OH concentration was available, but can be estimated from the HO<sub>2</sub> concentration formed in (R11) and (R12).

(R5) and (R6) are fast ( $k_5 = 5.5 \times 10^{-11}$  cm<sup>3</sup>s<sup>-1</sup> and  $k_6 = 9.6 \times 10^{-12}$  cm<sup>3</sup>s<sup>-1</sup> [35]), leading with typical concentrations of [CH<sub>3</sub>OH]  $\approx 8 \times 10^{14}$  cm<sup>-3</sup> and [O<sub>2</sub>] =  $1.1 \times 10^{17}$  cm<sup>-3</sup> to pseudo-first

order rates of  $k_5' = 4.4 \times 10^4 \text{ s}^{-1}$ , and  $k_6' = 1.1 \times 10^6 \text{ s}^{-1}$ , and are thus completed within few 10  $\mu\text{s}$ . No rate constants for the corresponding reactions with the deuterated species are available in the literature, and even though it can be expected that these reactions will be slower due to the kinetic isotope effect,  $\text{DO}_2$  will be equally formed on the  $\mu\text{s}$  time scale and will be in any case much faster than the peroxy self- and cross-reactions, which take place on the ms time scale. The ratio of  $[\text{HO}_2] / [\text{DO}_2]$  is given by the ratio of  $k_5 \times [\text{CH}_3\text{OH}] / k_7 \times [\text{CH}_3\text{OD}]$  (or  $k_9 \times [\text{CD}_3\text{OD}] / k_{11} \times [\text{CD}_3\text{OH}]$  respectively), whereby the last 2 terms are not known. However, a nearly linear increase of  $[\text{DO}_2]$  with increasing  $[\text{D}_2\text{O}]$  to the mixture  $\text{Cl}/\text{CH}_3\text{OH}/\text{O}_2$  was observed, while the fraction of  $\text{HO}_2$  radicals in a mixture  $\text{Cl}/\text{CD}_3\text{OD}/\text{O}_2$  decreased very rapidly upon addition of a small flow of  $\text{D}_2\text{O}$ . Examples for both experimental systems are shown in **Figure 2**: the left graph shows the percentage of Cl-atoms being converted to  $\text{DO}_2$  in a mixture  $\text{Cl}/\text{CH}_3\text{OH}/\text{D}_2\text{O}/\text{O}_2$  as a function of added  $[\text{D}_2\text{O}]$ , whereby the  $\text{DO}_2$  concentration is obtained as the difference in  $\text{HO}_2$  concentration before and after addition of  $\text{D}_2\text{O}$ . The right graph shows the percentage of Cl-atoms being converted to  $\text{HO}_2$  in a mixture  $\text{Cl}/\text{CD}_3\text{OD}/\text{D}_2\text{O}/\text{O}_2$  as a function of  $[\text{D}_2\text{O}]$ . Here,  $\text{HO}_2$  concentrations have been measured directly using the absorption cross sections,  $\text{DO}_2$  concentrations have been determined as explained further down.



**Figure 2:** Left graph: Fraction of Cl-atoms converted to  $\text{DO}_2$  as a function of added  $\text{D}_2\text{O}$  to a mixture  $\text{Cl}/\text{CH}_3\text{OH}/\text{D}_2\text{O}/\text{O}_2$ . Total pressure was 50 Torr,  $[\text{Cl}]_0 = 1.1 \times 10^{14} \text{ cm}^{-3}$ . Right graph: Remaining  $\text{HO}_2$  after adding different concentrations of  $\text{D}_2\text{O}$  to a mixture  $\text{Cl}/\text{CD}_3\text{OD}/\text{D}_2\text{O}/\text{O}_2$  in order to decrease concomitantly generated  $\text{HO}_2$ . Total pressure was 50 Torr,  $[\text{Cl}]_0 = 1.0 \times 10^{14} \text{ cm}^{-3}$ .

Experiments have been carried out in the pressure range 25 – 200 Torr, and initial  $[\text{Cl}]$  concentration varied typically between  $5 - 15 \times 10^{13} \text{ cm}^{-3}$ . The concentration of the excess isotope ( $\text{HO}_2$  or  $\text{DO}_2$ ) was typically in 5-10 times higher than the concentration of the other isotope ( $\text{DO}_2$  or  $\text{HO}_2$ ).



The gas flow into the photolysis reactor was controlled using calibrated flowmeters (Tylan FC-260). The main flows consisted of Helium and O<sub>2</sub> and were directly taken from the cylinder (both Alphagaz 2). The precursor Cl<sub>2</sub> was also directly taken from a commercial cylinder (5% Cl<sub>2</sub> in Helium, Alpha Gaz), CH<sub>3</sub>OH (CD<sub>3</sub>OD) was added to the gas mixture by flowing helium through a bottle containing liquid CH<sub>3</sub>OH (CD<sub>3</sub>OD) at room temperature, the concentration was estimated from the CH<sub>3</sub>OH vapor pressure, the total pressure in the bottle and the measured flow rate. D<sub>2</sub>O was either prepared as a mixture (2%) in a 20 l glass balloon and small concentrations were added through flowmeter in case of HO<sub>2</sub>-excess experiments or high concentrations were added by flowing a fraction of the main Helium through a bottle containing liquid D<sub>2</sub>O for DO<sub>2</sub>-excess experiments.

## Results and Discussion

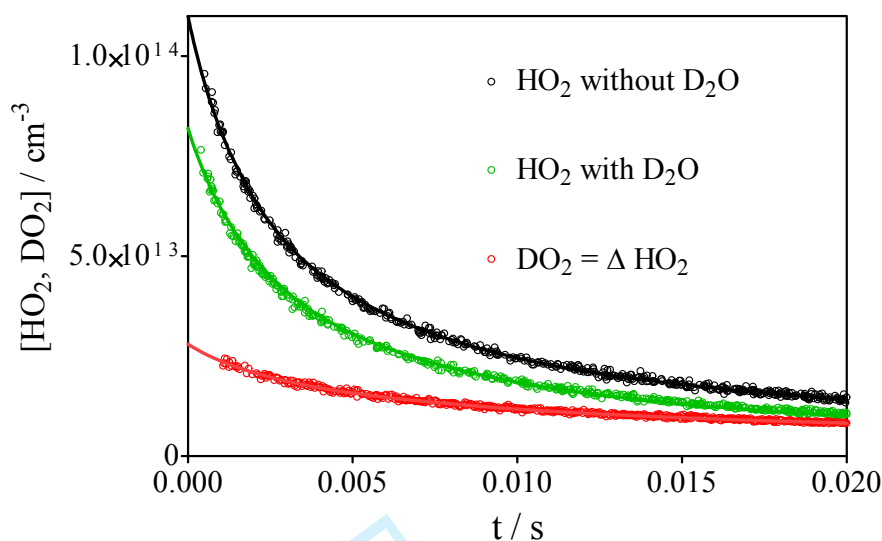
### Measurement of the rate constant of HO<sub>2</sub> + DO<sub>2</sub>

Experiments have been carried out under large excess of HO<sub>2</sub> over DO<sub>2</sub>. Under these conditions, the decay of the excess HO<sub>2</sub> is nearly exclusively governed by the rate constant for its self-reaction  $k_3$ , while for the DO<sub>2</sub> radical the self-reaction plays only a minor role due to lower concentrations and to a lower rate constant of the self-reaction  $k_2$ . Therefore, the DO<sub>2</sub> decay is governed nearly exclusively by their reaction with excess HO<sub>2</sub>; *i.e.* by the rate constant  $k_1$  and the absolute concentration of the HO<sub>2</sub> radical. These experimental conditions therefore result in a reliable determination of the rate constant of the cross reaction  $k_1$ , if the absolute HO<sub>2</sub> concentration can be determined. This is possible not only by converting the absorption-time profiles into concentration-time profiles using the well-known absorption cross sections [10,[21],[22],[23],[25],[26], but also by fixing  $k_3$  to the recommended literature value and subsequently adjusting the initial HO<sub>2</sub> concentration to best fit the HO<sub>2</sub> decay: both methods have been applied independently and led always to initial HO<sub>2</sub> concentration agreeing to better than +/-10% (see below). In other words: by choosing excess HO<sub>2</sub> concentration conditions, the rate constant  $k_1$  is measured relative to the well-known rate constant of the HO<sub>2</sub> self-reaction  $k_3$ . Any uncertainties in the absorption cross sections of HO<sub>2</sub> and DO<sub>2</sub> (the absorption lines are very narrow, especially at low pressure, and a small drift in the wavelength emitted by the DFB laser will result in a change of the effective absorption cross section) will not impact the retrieved rate constants  $k_1$ : the HO<sub>2</sub> absorption cross section is refined for each experiment by fitting the HO<sub>2</sub> decays to the fixed  $k_3$ , while the absolute

value of the absorption cross section of  $\text{DO}_2$  has only a very minor impact for retrieving  $k_1$ . These conditions minimize the uncertainty on  $k_1$ , because even if cross sections and pressure broadening factors of several strong absorption lines in the  $2\nu_1$  transition of  $\text{HO}_2$  have been well studied [10,[21],[22],[23],[25],[26], the rather small line at  $6638.58\text{ cm}^{-1}$ , that was used in this work in order to avoid saturation of the absorption due to the high initial radical concentrations, is less well known.

**Figure 3** shows a typical experiment at 50 Torr helium: the black trace shows the  $\text{HO}_2$  profile of an experiment in the absence of  $\text{D}_2\text{O}$ , the green trace shows the  $\text{HO}_2$  profile measured under the same conditions, but after addition of a small flow of  $\text{D}_2\text{O}$  to the gas flow; the red trace shows the corresponding  $\text{DO}_2$  profile measured simultaneously on the second cw-CRDS path. In a first step, the  $\text{HO}_2$  absorption profile in absence of  $\text{D}_2\text{O}$  is fitted to the literature value for the rate constant of the self-reaction,  $k_3$ , using a custom-designed Labview based program. This way the absorption cross section of  $\text{HO}_2$  can be retrieved at the given pressure. This step (measuring  $\text{HO}_2$  profiles in absence of  $\text{D}_2\text{O}$ ) is carried out at each pressure only for some  $\text{Cl}_2$  concentrations. In this work, we have used the rate constant for  $k_3$  in helium from Sander *et al* [1]. They have measured the pressure dependence of  $k_3$  for different bath gases ( $\text{He}$ ,  $\text{Ar}$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{SF}_6$ ) and their value for air (ie.  $0.2 \times k_{3,\text{O}_2} + 0.8 \times k_{3,\text{N}_2}$ ) is in excellent agreement with recommended values from IUPAC [36]. The reliability of  $k_3$  is estimated by the IUPAC committee to be  $\pm 40\%$ . Because all results in this work are determined relative to  $k_3$ , this uncertainty of  $\pm 40\%$  needs to be considered also for our  $k_1$  and  $k_2$  measurements. However, in what follows, we will only consider uncertainties occurring from our measurements and not add the uncertainty of  $k_3$ .

Once the  $\text{HO}_2$  concentration (and with this the absorption cross section) in absence of  $\text{DO}_2$  has been determined, the  $\text{HO}_2$  absorption time profile in presence of  $\text{D}_2\text{O}$  at the same  $\text{Cl}_2$  concentration is converted to a concentration-time profile using that absorption cross section. Now, the initial  $\text{DO}_2$  concentration can be calculated as the difference between both  $\text{HO}_2$  concentrations and hence the  $\text{DO}_2$  absorption cross section at the given pressure can be determined from the absorption at  $t = 0\text{ s}$ . Finally, the rate constant  $k_1$  is adjusted to best fit the  $\text{DO}_2$  profile.



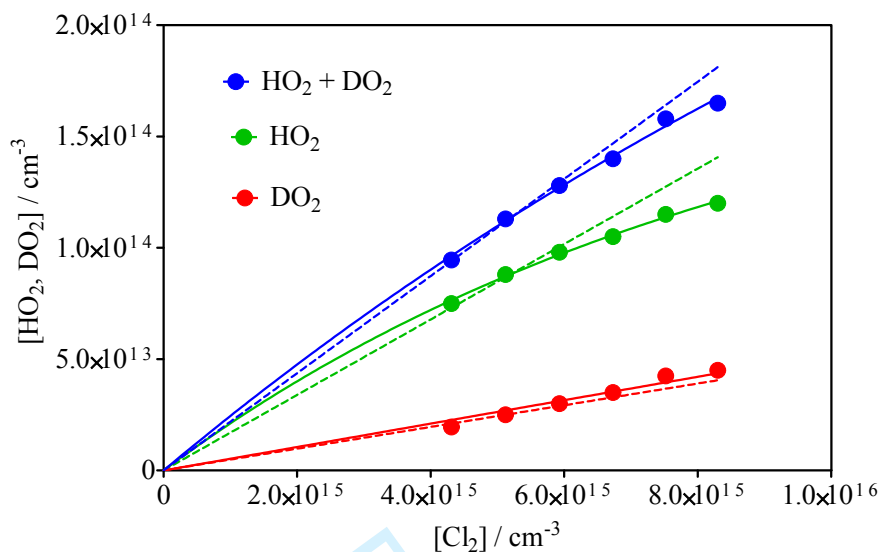
**Figure 3:** HO<sub>2</sub> concentration time profiles at 50 Torr in absence (black) and presence (green) of D<sub>2</sub>O and corresponding DO<sub>2</sub> profile (red) measured simultaneously (*i.e.* the red trace is not the difference between black and green). Initial HO<sub>2</sub> concentrations have been retrieved by fitting decay kinetics using  $k_3 = 1.58 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  [1], initial DO<sub>2</sub> concentration has been normalized as the difference in HO<sub>2</sub> concentration, the DO<sub>2</sub> decay has been fitted by adjusting  $k_1$ .

In practice, for retrieving the rate constant  $k_1$ , the HO<sub>2</sub> and DO<sub>2</sub> absorption profiles for a series of experiments at different Cl<sub>2</sub> concentrations (typically 6 at each pressure, see below) have initially all been converted to concentration-time profiles using the same absorption cross section obtained such as described above. However, HO<sub>2</sub> absorption lines are narrow, and a very minor deviation of the near IR-laser wavelength between different experiments can lead to a variation in the absorption cross section, especially for the low pressure experiments. Therefore, all 6 HO<sub>2</sub> and DO<sub>2</sub> concentration-time profiles have been fitted simultaneously using a very small mechanism consisting of (R1), (R2) and (R3) plus small losses due to diffusion of the radicals out of the photolysis volume. Unique rate constants for all reactions have been used for all different Cl-concentrations at each pressure. The individual HO<sub>2</sub> decays are very sensitive to the initial concentration (see below) and have been finely adjusted to best fit the unique rate constant  $k_3$ . The correction for the individual absorption cross sections was less than 10% for all experiments. The values for the absorption cross sections for HO<sub>2</sub>, averaged for each pressure over all experiments, and DO<sub>2</sub> obtained such as described above, are summarized in **Table 1**. Assuming a Voigt profile of the pressure broadened absorption lines, the integrated line strength and pressure broadening parameter have been determined from the data in **Table 1** with values leading for DO<sub>2</sub> (HO<sub>2</sub>) to a line strength of  $(6.8 \pm 0.7) \times 10^{-21}$  ( $(7.9 \pm 0.8) \times 10^{-22}$ ) cm and a broadening coefficient of 0.165 (0.06) cm<sup>-1</sup>/atm.

**Table 1:** Absorption cross sections of HO<sub>2</sub> and DO<sub>2</sub> for all pressures. Error bars contain only the uncertainty from our measurements, an additional uncertainty of  $\pm 40\%$  needs to be considered due to the uncertainty of  $k_3$  [36]

P / Torr	$\sigma_{\text{HO}_2} / 10^{-20} \text{ cm}^2$ at 6638.58 $\text{cm}^{-1}$	$\sigma_{\text{DO}_2} / 10^{-20} \text{ cm}^2$ at 7026.16 $\text{cm}^{-1}$
25	$3.3 \pm 0.3$	$20 \pm 2$
50	$2.8 \pm 0.3$	$13 \pm 1$
75	$2.4 \pm 0.2$	$12 \pm 1$
100	$2.1 \pm 0.2$	$9.3 \pm 0.9$
150	$1.7 \pm 0.2$	$6.3 \pm 0.6$
200	$1.4 \pm 0.1$	$4.5 \pm 0.4$

This type of experiment has been carried out at each pressure for a series of 6 different initial Cl<sub>2</sub> concentrations. The HO<sub>2</sub> and DO<sub>2</sub> concentrations as well as the sum of both radicals should increase linearly with increasing Cl<sub>2</sub> concentration. **Table 2** shows these data for a series of experiments at 50 Torr, and the values are plotted in **Figure 4**. The increase in radical concentration with Cl<sub>2</sub> is not perfectly linear (dashed line, forced through origin), but a slight saturation can be observed at the highest Cl<sub>2</sub> concentrations. This might be due to a fast reaction such as  $\text{Cl} + \text{CH}_2\text{OH}$  ( $k = 6.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ) [37], that starts to compete to (R6) or (R8) with increasing Cl concentration. Only one determination is available for the rate constant of the reaction  $\text{Cl} + \text{CH}_2\text{OH}$ , and such experiments could possibly be designed in a way (varying O<sub>2</sub> concentration at high Cl-concentration) to re-determine this rate constant, but is out of scope of this paper.

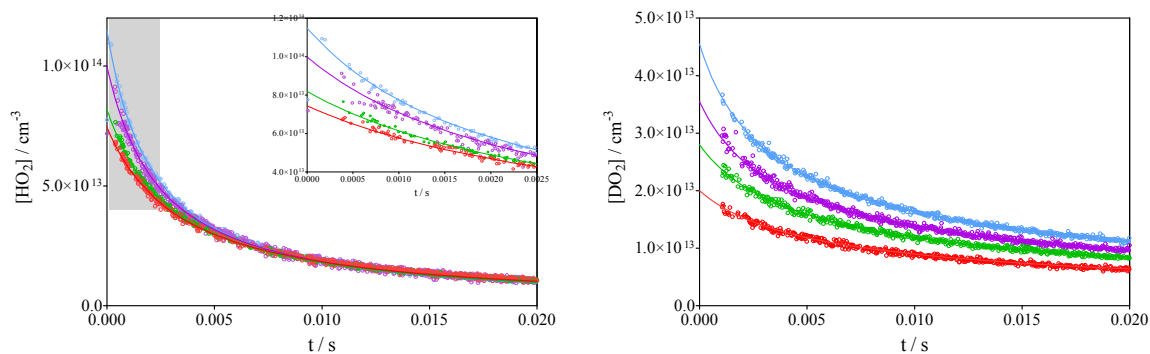


**Figure 4:** Data from **Table 2**, showing the initial  $\text{HO}_2$  (in presence of  $\text{D}_2\text{O}$ ),  $\text{DO}_2$  and sum of both as a function of  $\text{Cl}_2$  concentration

**Table 2:** Evolution of initial  $\text{HO}_2$  (in presence of  $\text{D}_2\text{O}$ ) and  $\text{DO}_2$  concentration with increasing  $\text{Cl}_2$  concentration, the example at 50 Torr

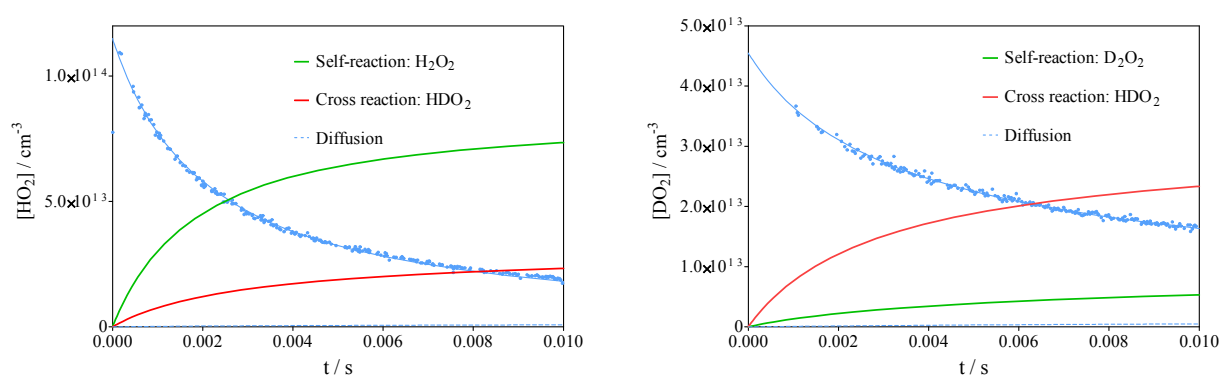
$\text{Cl}_2 / 10^{15} \text{ cm}^{-3}$	$\text{HO}_2 / 10^{14} \text{ cm}^{-3}$	$\text{DO}_2 / 10^{14} \text{ cm}^{-3}$	$\text{HO}_2 + \text{DO}_2 / 10^{14} \text{ cm}^{-3}$
8.30	1.20	0.45	1.65
7.52	1.15	0.43	1.58
6.73	1.05	0.35	1.40
5.93	1.0	0.30	1.28
5.12	0.9	0.25	1.15
4.31	0.8	0.20	1.0

**Figure 5** shows a series of  $\text{HO}_2$  and  $\text{DO}_2$  profiles with different  $\text{Cl}_2$  concentrations. For better visibility, the profiles of two intermediate  $\text{Cl}_2$  concentrations have been omitted. The full lines show the fit to the simple model containing (R1), (R2) and (R3) as well a loss through diffusion for each radical (very minor impact), using the rate constants from **Table 3**, the inset in the left graph shows a zoom on the  $\text{HO}_2$  profiles at short reaction times.



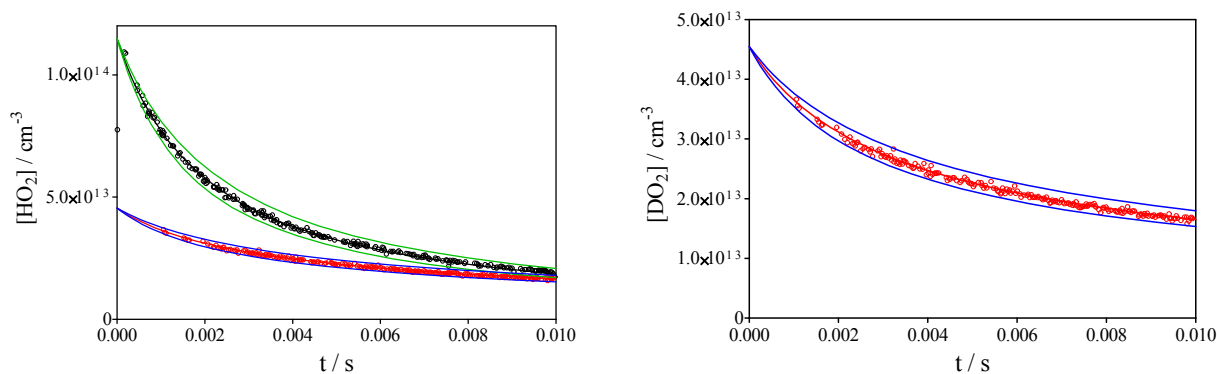
**Figure 5:** Typical series of experiments with increasing  $\text{Cl}_2$  concentration. Left graph:  $\text{HO}_2$  profiles, right graph  $\text{DO}_2$  profiles. The inset in the left graph shows a zoom of the  $\text{HO}_2$  profiles on the first 2.5 ms. No ring-down events occur during the first 1 ms on the  $\text{DO}_2$  absorption path, possibly due to perturbation of the DFB laser from scattered 351 nm photons. This phenomena is not observed when using 248 nm photolysis (see [29])

**Figure 6** shows the distribution of products for both reaction partners ( $\text{HO}_2$  on the left graph,  $\text{DO}_2$  on the right graph, green for self-reaction, red for cross reaction) for the experiment with the highest initial radical concentration from **Figure 5**: it can be seen that for  $\text{HO}_2$  the self-reaction is the major loss pathway, while for  $\text{DO}_2$  self-reaction is very minor and the decay is nearly exclusively governed by its reaction with  $\text{HO}_2$ .



**Figure 6:** Signal with highest  $\text{Cl}_2$  concentration from **Figure 5** with the loss through self-reaction (green line) and cross reaction (red line) for  $\text{HO}_2$  (left) and  $\text{DO}_2$  (right).

**Figure 7** shows the sensitivity of the signals to the rate constant  $k_I$ : the left graph shows both,  $\text{HO}_2$  (black) and  $\text{DO}_2$  (red), while  $\text{DO}_2$  is shown again on the right graph on a zoomed y-scale. The full lines show the best fit using the rate constants from **Table 3** and are barely visible, while for the upper and lower green lines the initial  $\text{HO}_2$  concentration in the model has been varied by  $\pm 20\%$  (*i.e.* simulating an uncertainty in the  $\text{HO}_2$  absorption cross section of  $\pm 20\%$ ). For better visibility, the simulated green curves have been multiplied by 1.2 / 0.8 to match the experimental data, rather than plotting three different experimental curves in which the absorption coefficient  $\alpha=f(t)$  would have been converted to  $[\text{HO}_2]=f(t)$  using three different absorption cross sections  $\sigma$ . It can be seen that the  $\text{HO}_2$  concentration-time profile is not well reproduced anymore with a 20% change in initial concentration, *ie.* at a fixed rate constant for the  $\text{HO}_2$  self reaction, the  $\text{HO}_2$  concentration can be determined to better than 20%. At the same time, the 20% change in initial  $\text{HO}_2$  concentration leads to a change of the  $\text{DO}_2$  concentration-time profile well outside the experimental uncertainty (blue lines).



**Figure 7:** Simulation showing the sensitivity to the initial HO<sub>2</sub> concentration for an experiment at 50 Torr. Black dots: experimental HO<sub>2</sub> concentration time profile, red dots: experimental DO<sub>2</sub> concentration time profile (zoomed in the right graph). Full lines (barely visible): fit to the model of **Table 3**, with the HO<sub>2</sub> concentration adjusted to best fit the decay, lower and upper green lines show variation of HO<sub>2</sub> profile with a +/- 20% change in initial concentration. For visual demonstration of the effect, the simulated green curves have been adapted to match the initial experimental HO<sub>2</sub> concentration, *ie.* have been multiplied by 1.2 / 0.8.

Final results for the rate constants  $k_1$  (and  $k_2$ , see below) for all different pressures are presented in **Figure 9** and **Table 3**. The rate constant for the cross reaction of HO<sub>2</sub> and DO<sub>2</sub> radicals can be given as pressure independent in the range 25 – 200 Torr helium as

$$k_1 = (1.6 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

The error bar includes an uncertainty of 10% from the fitting of the decays and an uncertainty of 10% for the rate constant of the HO<sub>2</sub> self reaction.

**Table 3:** Rate constants used to fit all experiments. Values  $k_2$  in **bold** are measured in absence of added D<sub>2</sub>O, values in *italic* are interpolated. Values for  $k_3$  are calculated from Sander et al. [1] with M = He

P / Torr	$k_1$ HO <sub>2</sub> + DO <sub>2</sub> / 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup>	$k_2$ DO <sub>2</sub> + DO <sub>2</sub> / 10 <sup>-13</sup> cm <sup>3</sup> s <sup>-1</sup>	$k_3$ HO <sub>2</sub> + HO <sub>2</sub> / 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup>	Diffusion / s <sup>-1</sup>
25	1.7±0.3	4.0±0.8	1.56	5
50	1.6±0.3	<b>4.1±0.8</b>	1.58	3
75	1.6±0.3	4.2±0.8	1.60	2
100	1.6±0.3	<b>4.3±0.8</b>	1.61	1
150	1.6±0.3	4.4±0.8	1.65	1
200	1.6±0.3	<b>4.5±0.8</b>	1.69	0



### Measurement of the rate constant $k_2$ for the reaction $\text{DO}_2 + \text{DO}_2$

Determining the rate constant for the  $\text{DO}_2$  self-reaction,  $k_3$ , requires knowledge of the absolute  $\text{DO}_2$  concentration. However, only very little is known about absolute absorption cross sections and pressure broadening in the near infrared [29]. Therefore, two different methods can be used for determining the  $\text{DO}_2$  concentration. (a) the Cl-atom concentration is initially determined by adding  $\text{CH}_3\text{OH}$  and thus transforming them quantitatively into  $\text{HO}_2$  radicals. After switching to  $\text{CD}_3\text{OD}/\text{D}_2\text{O}$  mixtures, the  $\text{DO}_2$  and  $\text{HO}_2$  absorption time profiles are determined, and the initial  $\text{DO}_2$  concentration (and thus the absorption cross section) can be determined under the hypothesis that the Cl-atom concentration has not changed. This is equivalent to the above described method. (b) Fitting the  $\text{HO}_2$  decays in presence of excess  $\text{DO}_2$  to the reaction system (R1) – (R3) and fixing the rate constant  $k_1$  to the above obtained value. Now the  $\text{HO}_2$  decay will depend on the initial  $\text{DO}_2$  concentration. Both methods (a) and (b) have been applied independently and have returned values for the initial  $\text{DO}_2$  concentrations that agreed to better than 15% to each other. The so-obtained absorption cross section for  $\text{DO}_2$  was then used to convert absorption time profiles into absolute  $\text{DO}_2$  concentration time profiles, and to determine the rate constant for the  $\text{DO}_2$  self-reaction.

In order to minimize the  $\text{HO}_2$  concentration that is always formed through (R11) and (R12),  $\text{D}_2\text{O}$  has been added to the gas flow by flowing a fraction of the bath gas Helium through a bubbler containing  $\text{D}_2\text{O}$ . The fraction of Cl-atoms being converted to  $\text{HO}_2$  decreased rapidly from around 30% in absence of any added  $\text{D}_2\text{O}$  over 8% in presence of  $[\text{D}_2\text{O}] \approx 6 \times 10^{15} \text{ cm}^{-3}$  to less than 2% with  $[\text{D}_2\text{O}] \approx 3.5 \times 10^{16} \text{ cm}^{-3}$  (see **Figure 2**).

It was observed that both rate constants,  $k_1$  and  $k_2$ , increased with increasing  $\text{D}_2\text{O}$  concentration, as shown in **Figure 8**. This is in agreement with observations for an increase in  $k_2$  with increasing  $\text{H}_2\text{O}$  concentration.

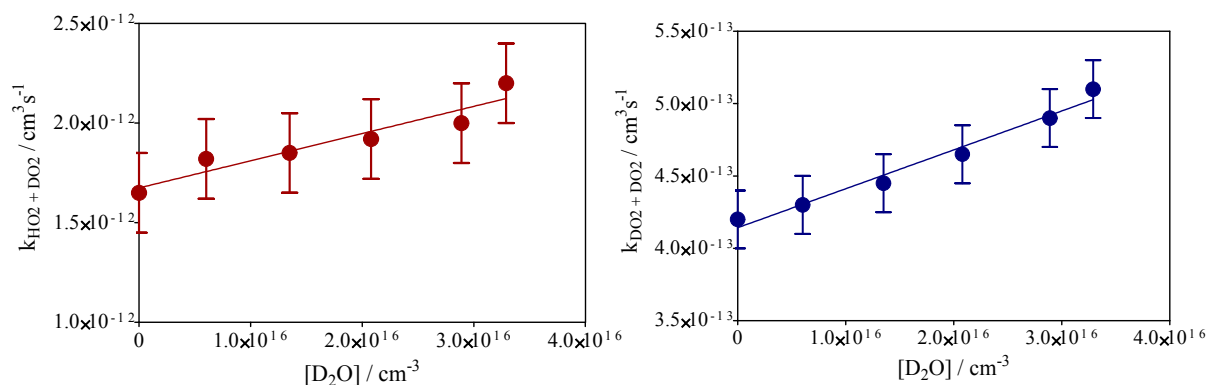
$$k_1 = (1.67 \pm 0.03) \times 10^{-12} \times (1 + (8.2 \pm 1.6) \times 10^{-18} \text{ cm}^3 \times [\text{D}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$$

$$k_2 = (4.14 \pm 0.02) \times 10^{-13} \times (1 + (6.5 \pm 1.3) \times 10^{-18} \text{ cm}^3 \times [\text{D}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$$

Error bars represent statistical error only for intercept and an addition error of 10% for uncertainty in the  $\text{D}_2\text{O}$  concentration. The effect observed in this work with  $\text{D}_2\text{O}$  is 2 to 3 times larger than the effect with  $\text{H}_2\text{O}$ , which has been found by Kircher and Sander [2] to be

$$k_3 = 1.6 \times 10^{-12} \times (1 + 2.25 \times 10^{-18} \text{ cm}^3 \times [\text{H}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$$



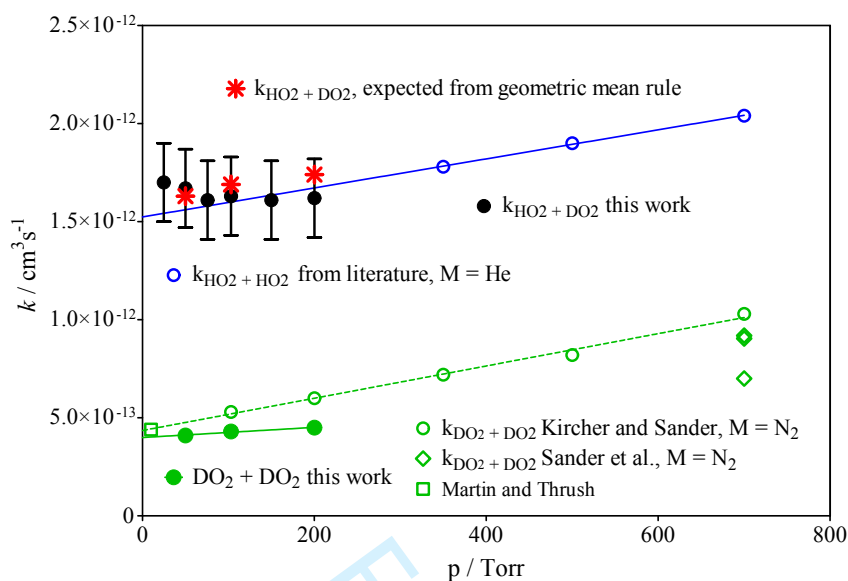


**Figure 8:** Rate constants  $k_1$  (left) and  $k_2$  (right) as a function of  $D_2O$  concentration.

Measurements have been carried out at 50, 100 and 200 Torr (values are given in **bold** in **Table 3**) and insignificant pressure dependence is observed:

$$k_2 = (4.1 \pm 0.6) \times 10^{-13} (1 + (2 \pm 2) \times 10^{-20} \text{ cm}^3 \times [\text{He}] \text{ cm}^{-3}) \text{ cm}^3 \text{s}^{-1}$$

The error bars represent statistical error only, the systematic error due to the uncertainty in  $k_3$  is not taken into account. The data are plotted in **Figure 9**, together with the values for  $k_1$  as obtained in this work, and  $k_2$  from literature. No data for  $k_2$  in helium could be found in the literature, but extrapolation to  $p = 0$  shows a very good agreement of the current results with literature data. Interestingly, in the work of Sander et al,  $k_2$  has been measured at 760 Torr using 2 different precursors: either using  $\text{Cl}_2$  photolysis in the presence of  $\text{CD}_3\text{OD}/\text{O}_2$  or in the presence of  $\text{D}_2/\text{O}_2$ . The rate constant they obtained using the first system, was significantly higher than when they used the second system, a difference which was considered by the authors beyond experimental uncertainty and could not be unexplained. A possible explanation would be that in their experiments residual  $\text{H}_2\text{O}$  was also present, which led to some  $\text{HO}_2$  next to the desired  $\text{DO}_2$ . However, their detection method (UV-absorption spectroscopy) did not allow distinguishing  $\text{DO}_2$  from  $\text{HO}_2$ , and thus the signal represented the sum of  $\text{HO}_2$  and  $\text{DO}_2$  and the decay was partially due to the faster reaction of  $\text{DO}_2$  with  $\text{HO}_2$ . When using  $\text{D}_2$  as precursor, no formation of  $\text{HO}_2$  is expected, and the observed decay is only due to the slower  $\text{DO}_2$  self-reaction.



**Figure 9:** Rate constants  $k_1$  ( $\text{HO}_2 + \text{DO}_2$ , black dots) and  $k_2$  ( $\text{DO}_2 + \text{DO}_2$ , green dots) from this work. Literature data for  $k_2$ : open circles from Kircher and Sander [2], open diamonds from Sander *et al.* [1] and open square from Martin and Thrush [17]. Red symbols show  $k_1$  such as expected from geometrical rule, taking  $k_2$  from this work and  $k_3$  from Kircher and Sander [2] (blue symbols).

The geometric mean rule is an empirical approach that allows for the estimation of cross-reaction rate coefficients from the self-recombination rate constants of the reacting partners [38]

$$k_{A+B} = 2 \times \sqrt{k_{A+A} \times k_{B+B}}$$

It has shown to work to better than 20% in the prediction of radical-radicals rate coefficients for a series of hydrocarbon radicals [39]. In absence of any literature data for  $k_1$ , we have tentatively applied this rule to estimate  $k_1$  by using the literature values for  $k_3$  and the values for  $k_2$  such as obtained in this work. In **Figure 9** are shown as red stars the values for  $k_1$  obtained this way: excellent agreement is found with our experimental determinations.

## Conclusion

The rate constant of the cross reaction between  $\text{HO}_2$  and  $\text{DO}_2$  radicals has been measured for the first time thanks to a simultaneous and selective measurement of absolute concentrations of  $\text{HO}_2$  and  $\text{DO}_2$  radicals by time resolved cw-CRDS in the near infrared. The rate constant was determined under conditions where the  $\text{HO}_2$  radical was in excess over the  $\text{DO}_2$  radical. Under these conditions, the decay of  $\text{DO}_2$  is essentially given by the absolute concentration of  $\text{HO}_2$  radicals and the rate constant  $k_1$ . The  $\text{HO}_2$  concentration in turn can be determined by

fitting its decay, which is essentially governed by its self-reaction. The rate constant  $k_I$  has been found independent on pressure in the range 25 – 200 Torr helium, but increasing with added D<sub>2</sub>O:

$$k_I = (1.67 \pm 0.03) \times 10^{-12} \times (1 + (8.2 \pm 1.6) \times 10^{-18} \text{ cm}^3 \times [\text{D}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$$

The rate constant for the self reaction of DO<sub>2</sub> has been determined by quantifying the DO<sub>2</sub> concentration in two different ways: either Cl-atoms were initially converted to HO<sub>2</sub> radicals (which can be quantified by cw-CRDS) by addition of CH<sub>3</sub>OH which can be quantified. Then CH<sub>3</sub>OH was replaced by CD<sub>3</sub>OD, and it was considered that the Cl-atom concentration had not changed. In an independent method, the decay of the remaining small concentration of HO<sub>2</sub> radicals next to the excess DO<sub>2</sub> radicals was fitted using the above determined rate constant  $k_I$ . Both methods gave consistent concentrations and led to a rate constant with insignificant pressure dependence for the self-reaction of DO<sub>2</sub>, in good agreement with the available literature data:

$$k_2 = (4.1 \pm 0.6) \times 10^{-13} (1 + (2 \pm 2) \times 10^{-20} \text{ cm}^3 \times [\text{He}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$$

For this reaction also, an increase of  $k_2$  with increasing concentration of D<sub>2</sub>O was found:

$$k_2 = (4.14 \pm 0.02) \times 10^{-13} \times (1 + (6.5 \pm 1.3) \times 10^{-18} \text{ cm}^3 \times [\text{D}_2\text{O}] \text{ cm}^{-3}) \text{ cm}^3 \text{ s}^{-1}$$

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