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OH, HO₂, and Ozone Gaseous Diffusion Coefficients

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The diffusion of OH, HO₂, and O₃ in He, and of OH in air, has been investigated using a coated-wall flow tube reactor coupled to a chemical ionization mass spectrometry. The diffusion coefficients were determined from measurements of the loss of the reactive species to the flow tube wall as a function of pressure. On the basis of the experimental results, $D_{\text{OH-He}} = 662 \pm 33 \text{ Torr cm}^2 \text{ s}^{-1}$, $D_{\text{OH-air}} = 165 \pm 20 \text{ Torr cm}^2 \text{ s}^{-1}$, $D_{\text{HO}_2\text{-He}} = 430 \pm 30 \text{ Torr cm}^2 \text{ s}^{-1}$, and $D_{\text{O}_3\text{-He}} = 410 \pm 25 \text{ Torr cm}^2 \text{ s}^{-1}$ at 296 K. We show that the measured values for OH and HO₂ are in better agreement with measured values of their polar analogues (H₂O and H₂O₂) compared with measured values of their nonpolar analogues (O and O₂). The measured value for OH in air is 25% smaller than that for O (the nonpolar analogue). The difference between the measured value for HO₂ and O₂ (the nonpolar analogue) in air is expected to be even larger. Also we show that calculations of the diffusion coefficients based on Lennard–Jones potentials are in excellent agreement with the measurements. This gives further confidence that these calculations can be used to estimate accurate diffusion coefficients for conditions where laboratory data currently do not exist.

Introduction

Research over the past 20 years has shown that reactions between trace gas-phase species and aerosol particles and cloud droplets (termed heterogeneous chemistry) play an important role in the atmosphere. OH, HO₂, and O₃ are examples of trace gas-phase species that can undergo important heterogeneous reactions in the atmosphere. For example, it has recently been shown that OH radicals can oxidize organic particles, and this reaction may be an important loss process of organic material in the atmosphere.^{1,2} Also, reactions of both OH and HO₂ (also called HO_x) with cloud droplets play an important role in cloud chemistry.^{3–8} Other heterogeneous reactions that are thought to be important include HO_x uptake on sea salt particles^{9–11} and cirrus clouds^{12–16} and O₃ uptake on fresh soot particles. In the later case, O₃ is thought to oxidize the soot particles and hence change the hygroscopic properties of soot particles, which may affect the soot lifetime in the atmosphere under certain conditions.¹⁷

The loss of gas-phase species to atmospheric particles and cloud droplets can be controlled by both diffusion to the particle/droplet surface or the reaction rate at the particle/droplet surface. The overall rate constant for heterogeneous loss, k_{obs} , to a particle/droplet surface can be described by the following equation (which is based on rule of the additivity of kinetic resistances¹⁸):

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{het}}} + \frac{1}{k_{\text{dif}}} \quad (1)$$

where k_{het} is the kinetic rate constant of heterogeneous loss which depends on an uptake coefficient and the mean thermal velocity and k_{dif} is the diffusion rate constant to the particle/droplet surface. k_{dif} can be described by the following equation:⁵

$$k_{\text{dif}} = \frac{3D_g}{r_p^2} V = 4\pi r_p D_g n \quad (2)$$

where D_g is the gas-phase diffusion coefficient, V is the particle volume, and n is the aerosol number density. Combining eq 1 and 2 gives the following equation:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{het}}} + \frac{1}{4\pi r_p D_g n} \quad (3)$$

Equation 3 shows that in order to predict the observed first-order loss rate of gas-phase species, such as OH, HO₂, and O₃, to atmospheric particles and droplets, knowledge of the diffusion coefficient is required.

In laboratory studies, knowledge of diffusion coefficients is also required to accurately determine reactive uptake coefficients (i.e., reaction probabilities) of trace species onto atmospherically relevant surfaces. In other words, when determining reactive uptake coefficients of gas-phase species in the laboratory, one often needs to correct for concentration gradients in the experiments, which require accurate diffusion coefficients of the species under investigation.

Despite the importance of diffusion coefficients for predicting the heterogeneous loss of gas-phase species on atmospheric particles and cloud droplets and also for analyzing laboratory data, accurate values of this parameter in many cases do not

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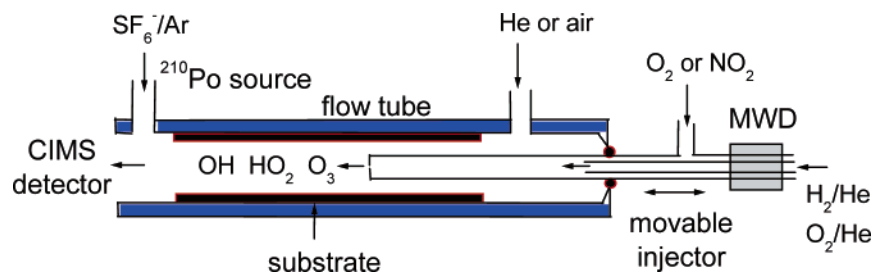


Figure 1. Schematic diagram of the fast flow-tube reactor coupled to CIMS.

exist. This is especially true for OH, HO₂, and O₃. In air or He, there has been only one measurement for HO₂,⁹ no measurements for O₃, and two measurements for OH.^{1,12} Furthermore, in one of the two previous OH studies, there was a large uncertainty associated with the measurement. Clearly more work in this area is required.

In the following we measured the diffusion of OH, HO₂, and O₃ in He, and OH in air. Note that measurements in He are beneficial since most laboratory studies of reactive uptake coefficients use He as a carrier gas, and hence, these laboratory studies require the diffusion coefficient of OH in He to analyze their laboratory data. Also, measurements of diffusion coefficients in He can be used to test theoretical calculations.

In addition to measuring diffusion coefficients, we have compared the diffusion coefficients for OH and HO₂ with the measured diffusion coefficients of their nonpolar analogues (O and O₂) and the measured diffusion coefficients of the polar analogue (H₂O and H₂O₂). In the past, researchers have used the nonpolar analogues to estimate the diffusion coefficients of OH and HO₂. Our comparison shows that the diffusion coefficients of OH and HO₂ are closer to their polar analogues than the nonpolar analogues, and hence the nonpolar analogues should not be used for estimate the transport properties of OH and HO₂, rather the polar analogues should be used (or calculations based on the polar analogues) when no direct measurements of the diffusion coefficients of OH and HO₂ are available.

In addition we compared our results for OH, HO₂, and O₃ to calculations of the diffusion coefficients based on the Lennard-Jones potential. For OH and HO₂, we used the collision parameters of the polar analogues. We show the calculations are in excellent agreement with the measurements, and hence this model can be used to predict diffusion coefficients accurately for conditions where no laboratory data exist.

Experimental Section

To determine diffusion coefficients of HO_x and O₃, we measured the first-order loss rate of these species to reactive surfaces as a function of pressure using a coated-wall flow tube reactor. Then the pressure dependent data were analyzed using the rule of additivity of kinetic resistances to yield diffusion coefficients.

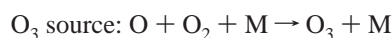
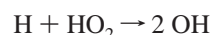
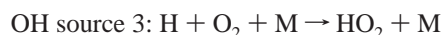
The first-order loss rates of HO_x and O₃ to various reactive surfaces as a function of pressure were determined using a coated-wall flow tube reactor coupled to a chemical ionization mass spectrometer (see Figure 1).^{1,2,19} The flow tube, 2.5 cm i.d. by 25 cm long, was constructed of borosilicate glass and included a movable injector through which OH, HO₂, or O₃ was introduced. Helium or air, the main carrier gas, was introduced through a port at the upstream end of the flow reactor. All flow rates were determined with calibrated electronic mass flow meters (Tylan General) or by monitoring the rate of change of pressure in a known volume. Typical conditions in the flow

tube were 12–40 m s⁻¹ flow velocity of He or air at 1.0–6.3 Torr. A typical experiment consisted of measuring the OH, HO₂, or O₃ signal as a function of injector position. The signal was then plotted as a function of reaction time to determine the first-order loss rate coefficient, k_{obs} , at the flow tube wall. This whole process was then repeated at various pressures to obtain k_{obs} as a function of pressure.

A movable injector was used as a radical (OH, HO₂) or O₃ source. The following reactions were used to generate the species:

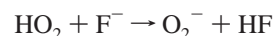
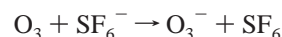
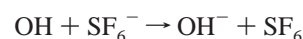


(a microwave discharge of H₂O vapor in He)



See references 1 and 2 for more details on the HO_x and O₃ sources. Typical HO_x and O₃ concentrations were less than 10¹⁰ molecule cm⁻³. Under these conditions the gas-phase secondary chemistry was not important.

For the CIMS measurements, SF₆⁻ was used as the reagent ion for detection of O₃ and OH, and F⁻ was used as the reagent ion for detection of HO₂. The following equations describe the important chemistry:



SF₆⁻ and F⁻ were produced by combining trace amounts of SF₆ and F₂, respectively, with Ar and then passing the mixture through a ²¹⁰Po ion source. The CIMS sensitivity was found to be ~ 10⁶ molecules cm⁻³ for OH, 2·10⁶ molecules cm⁻³ for HO₂, and ~ 10⁸ molecules cm⁻³ for O₃ at S/N = 1 and an integration time of 1 s.

The following reactive surfaces were used when determining k_{obs} as a function of pressure: for OH, an Al₂O₃ surface ($\gamma_{\text{OH}} = 0.2$) and octadecyltrichlorosilane (OTS), ($\gamma_{\text{OH}} \sim 1$) were used. [The values in the brackets represent the reaction probability or reactive uptake coefficient of the trace gas-phase species on the reactive surface.]^{1,2} For HO₂, an Al₂O₃ surface ($\gamma_{\text{HO}_2} = 0.013$) and methane-soot ($\gamma_{\text{HO}_2} = 0.05$) surface was used. Finally, for O₃, a methane-soot surface ($\gamma_{\text{O}_3} = 0.033$) was used. The uptake coefficient of O₃ on methane soot in round brackets was determined in the present experiments, where all other

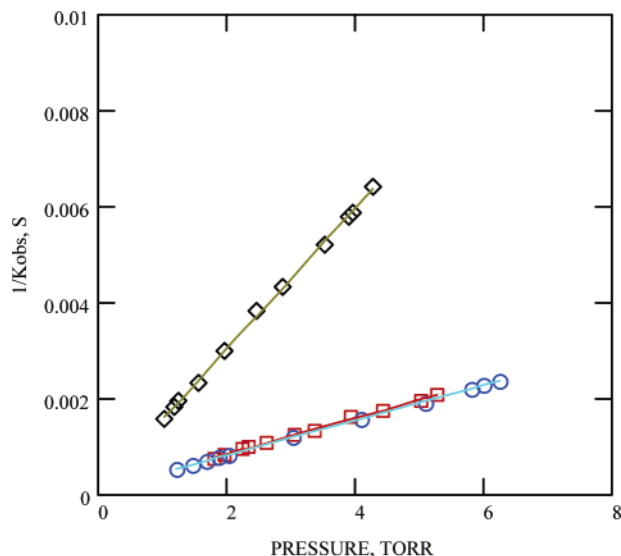


Figure 2. The pressure dependence of $1/k_{\text{obs}}$ of OH loss on Al_2O_3 (squares) and OTS (circles) in He and on Al_2O_3 (diamonds) in air. The solid lines are a linear least-squares fit to the data.

uptake coefficients were determined in previous measurements.¹⁹ The methods of preparation of the surfaces are described in detail elsewhere.^{1,2} In short, for the soot and OTS monolayer, a pyrex cylindrical tube was coated with the material and then inserted into the flow tube reactor. For the Al_2O_3 and graphite surfaces, a cylindrical tube constructed of Al_2O_3 and graphite, respectively, was inserted into the flow reactor.

The gases employed were He (BOC, 99.999%), synthetic air (BOC, grade 0.2), and NO_2 (Matheson, 99.5%). The surface materials used were Al_2O_3 (Aldrich, 99.9%), OTS (Aldrich, >90%), graphite (Aldrich, 99.9%), and methane soot produced from a methane-air flame.

As mentioned above, we determined the first-order loss rate (specifically the first-order loss rate coefficient, k_{obs}) of HO_x and O_3 on the reactive surfaces as a function of pressure. The data were then analyzed using the rule of additivity of kinetic resistances to determine diffusion coefficients. For a cylindrical reactor, the observed first-order loss rate coefficient at the flow tube wall, k_{obs} , can be described by the following equation:²⁰

$$\frac{1}{k_{\text{obs}}} = \frac{2r}{\gamma c_{\text{avg}}} + \left(\frac{r^2}{3.66D_p} \right) p \quad (4)$$

where p is the pressure (Torr), r is the radius of the flow tube reactor (cm), and D_p is the diffusion coefficient ($\text{Torr cm}^2 \text{s}^{-1}$). According to eq 4, a plot of $1/k_{\text{obs}}$ versus pressure gives a straight line with the slope inversely proportional to the diffusion coefficient. Also, the reactive uptake coefficient can be determined from the intercept. In our analysis, $1/k_{\text{obs}}$ was plotted as a function of pressure, and the diffusion coefficient was determined from the slope. The diffusion coefficients determined with this method were independent of the reactive uptake coefficient.

Results and Discussion

Prior to measuring the diffusion coefficients of HO_x and O_3 , we first measured the diffusion coefficient of atomic oxygen in He, as a validation of our apparatus and method of data analysis. The diffusion coefficient of O has been measured in the past by several others, and hence represents a good test for our apparatus and methodology. Shown in Figure 4 is the depen-

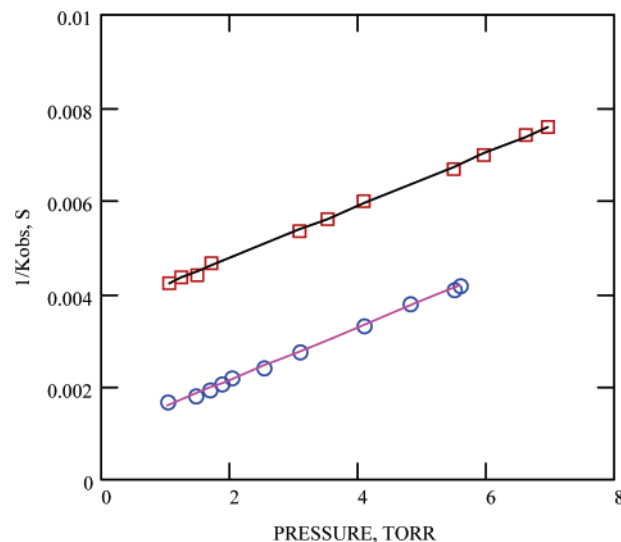


Figure 3. The pressure dependence of $1/k_{\text{obs}}$ of HO_2 loss on Al_2O_3 (squares) and soot (circles) in He. The solid lines are a linear least-squares fit to the data.

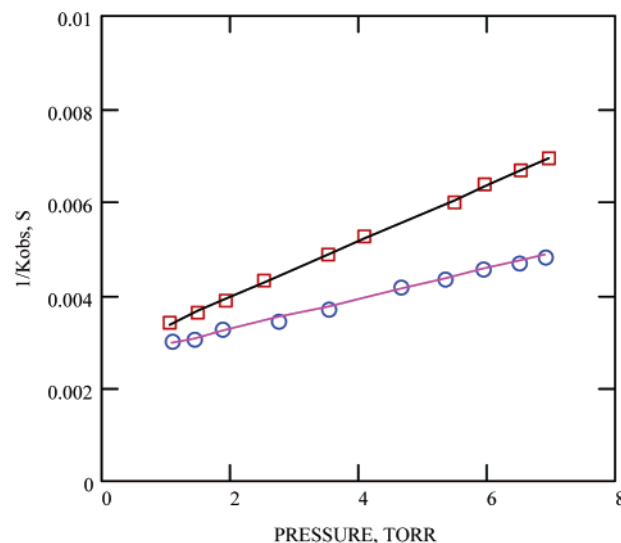


Figure 4. The pressure dependence of $1/k_{\text{obs}}$ of O_3 loss on soot (squares) and of O loss on graphite (circles) in He. The solid lines are a linear least-squares fit to the data.

dence of the first-order loss rate constant of O on a graphite surface using a He carrier gas. From the slope of this plot, the following diffusion coefficient was obtained: $D_{\text{O-He}} = 756 \pm 40 \text{ Torr cm}^2 \text{s}^{-1}$. The experimental finding is quite consistent with literature values, which range from 731 to 815 $\text{Torr cm}^2 \text{s}^{-1}$.^{21–23} Note, that we have not considered the data reported in reference 31 when determining this range due to the criticisms reported in reference 22.

Measurements of the Diffusion Coefficients of HO_x and O_3 and Comparison with Previous Measurements. Shown in Figure 2 is a plot of the typical pressure dependences of the observed first-order loss rate coefficient of OH on Al_2O_3 and OTS surfaces with He as a carrier gas. Both dependences reveal very close values of $657 \pm 25 \text{ Torr cm}^2 \text{s}^{-1}$ and $674 \pm 25 \text{ Torr cm}^2 \text{s}^{-1}$ using the inorganic and organic surfaces. Based on our measurements of the diffusion coefficient, the average value is $D_{\text{OH-He}} = 662 \pm 33 \text{ Torr cm}^2 \text{s}^{-1}$. Figure 2 also shows the pressure dependence in synthetic air. The diffusion coefficient determined from this plot is $D_{\text{OH-air}} = 163 \pm 20 \text{ Torr cm}^2 \text{s}^{-1}$. Figure 3 illustrates the similar pressure-dependent heterogeneous loss of HO_2 on Al_2O_3 and methane-soot surfaces. The measured

TABLE 1: Diffusion Coefficients of OH, HO₂ and O₃ at 1 Torr and 296 K

| partner 1 | partner 2 | D_{12} , cm ² s ⁻¹ | ref |
|----------------------------|-----------|--------------------------------------------|------------|
| OH ($X^2\Pi$) | He | 662 ± 33 | this study |
| | | 609 ± 250 | 24 |
| | | 665 ± 35 | 1 |
| HO ₂ (X^2A) | air | 163 ± 20 | this study |
| | He | 430 ± 30 | this study |
| | | 405 ± 50 | 25 |
| O ₃ (1A_1) | He | 410 ± 25 | this study |

diffusion coefficients are $D_{\text{HO}_2\text{-He}} = 430 \pm 30$ Torr cm² s⁻¹ for both surfaces. The dependences of O₃ loss on the methane-soot surface in He are shown in Figure 4. The value obtained is $D_{\text{O}_3\text{-He}} = 410 \pm 25$ Torr cm² s⁻¹.

The results from our measurements together with previous measurements of HO_x diffusion coefficients are summarized in Table 1.^{1,24,25} The previous measurements also used the rule of additivity of kinetic resistances and flow tube reactors to determine diffusion coefficients.^{1,9,26} The data summarized in Table 1 show that our measurements are consistent with previous measurements, and also highlight the fact that the measurements reported in this study significantly expand the available data on the diffusion coefficients of OH, HO₂ and O₃.

Surprisingly, to date there have been no direct measurements for the O₃ diffusion coefficient in He or air. An experimental assessment,²⁷ where the diffusion coefficient of O₃ in air was inferred from a complex system of reactions, produced an estimated value of 230 to 460 Torr cm² s⁻¹ at room temperature. There are also two theoretical estimates^{28,29} of the O₃ diffusion coefficient in O₂, which range from 91 to 205 Torr cm² s⁻¹ at 298–300 K. Also, there is an estimate³⁰ of 394 Torr cm² s⁻¹ for the O₃ diffusion coefficient in He at 298 K based on averaging the diffusion coefficients of stable molecules SO₂, CO₂, and NOCl, which is in reasonable agreement with our measured value. This latter value has been used in the past when analyzing laboratory measurements of reactive uptake coefficients.³⁰

Comparison between Measured Diffusion Coefficients of HO_x and Measured Diffusion Coefficients of Polar and Nonpolar Analogues. In the past, researchers have used the diffusion coefficients of O and O₂ (nonpolar analogues for OH and HO₂, respectively) to approximate the diffusion coefficients of OH and HO₂.^{6,13} In Table 2 we compare our measured diffusion coefficients of HO_x with the measured diffusion coefficients of the nonpolar analogues (O and O₂)^{21–23,31–39} as well as measured diffusion coefficients of the polar analogues (H₂O and H₂O₂).^{40–43} The measured diffusion coefficients for OH in He are in much better agreement with the polar analogue (H₂O) than the nonpolar analogue (O). The measured diffusion coefficient for OH in air also appears to follow a similar trend, although definitive conclusions are not possible due to the large

uncertainty in the measured diffusion coefficients of H₂O in air. In addition, OH diffusion differs from that of O by 11% in He and by 25% in air. From the HO₂ data, we can also conclude that the measured diffusion coefficient of HO₂ in He is not in good agreement with the measured diffusion coefficient of the nonpolar analogue (O₂) in He: HO₂ diffusion is approximately 28% lower compared to O₂ in He. Based on this, we conclude that the nonpolar analogue should not be used for estimate the transport properties of OH and HO₂, rather the polar analogues should be used (or calculations based on the polar analogues; see below) when no direct measurements of the diffusion coefficients of OH and HO₂ are available. Note this conclusion has been made previously in the literature based on a limited data set.^{1,9} Our results provide stronger support for this conclusion.

The trend observed in Table 2 can be rationalized with the dipole moments of the molecules or atoms. The dipole moments of OH and HO₂ are 1.74⁴⁴ and 2.090 ± 0.034,⁴⁵ respectively. The dipole moments of H₂O and H₂O₂ are 1.82⁴⁶ and 2.13 ± 0.05,⁴⁶ respectively, whereas the dipole moment of O and O₂ are both zero. A radical has a smaller diffusion coefficient than its nonpolar analogues since the radical diffusion is determined for the most part by the anisotropy of the atom–radical and molecule–radical interaction potentials, which is related to the dipole moments. For example, the anisotropy of interactions involving both OH and H₂O are certainly much larger than those of interactions involving O atoms, due to the dipole moments. This result also applies to HO₂ and H₂O₂ versus O₂. In addition, the presence of the body-fixed dipole moment in OH, H₂O, HO₂, and H₂O₂ makes the interactions involving these species much stronger. As a result, HO_x radical diffusion is expected to be slower in both nonpolar and polar gases.

Comparisons between the Measured Diffusion Coefficients and Calculations based on the 6–12 Lennard–Jones Potential Model. When calculating diffusion coefficients, we used the 6–12 Lennard–Jones potential model⁴⁷ to describe the interactions between gas-phase species:

$$\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

where $\varphi(r)$ is the 6–12 Lennard–Jones potential and r is the distance between two molecules. This model describes reasonably well the interaction between simple nonpolar molecules and includes the following two parameters: σ (the collision diameter at $\varphi(r) = 0$) and ϵ (the potential well depth where the attraction energy is maximum $r = 2^{1/6}\sigma$), which are constants characteristic of the colliding molecules.

In kinetic theory of dilute gases, a transport coefficient such as a diffusion coefficient is expressed in terms of a set of reduced collision integrals, which in turn depend on the potential model that describes the molecular interaction. Within the Lennard–

TABLE 2: Comparison between Our Measured Diffusion Coefficients of HO_x and Measured Diffusion Coefficients of the Nonpolar and Polar Analogues

| partner 1 | partner 2 | measured (this study) | measured diffusion coefficient of the polar analogues | measured diffusion coefficient of the nonpolar analogue |
|-----------------|-----------|-----------------------|-------------------------------------------------------|---------------------------------------------------------|
| OH | He | 662 ± 33 | 646–690 ^a | 731–815 ^b |
| | air | 163 ± 20 | 154–241 ^c | 205–243 ^d |
| HO ₂ | He | 430 ± 30 | ND | 538–559 ^e |
| | Air | ND | 111–116 ^f | 158–175 ^g |

^a Based on refs 40–42. ^b Based on refs 21–23, we have not considered the data reported in reference 31 when determining this range due to the criticisms reported in reference 22. ^c Based on refs 41–42. ^d Based on the diffusion in O₂ reported in refs 21, 31, 32 [note, the diffusion in O₂ is expected to be within a few percent of the diffusion in air]. ^e Based on refs 33–36. ^f Extrapolated from ref 43 using a T^{1.92} dependence; the temperature dependence was determined by first calculating the diffusion coefficient of H₂O₂ in air for temperatures ranging from 20 to 5000 K and then by fitting the temperature-dependent data. ^g Based on the diffusion in N₂, reported in refs 32, 37–39; ND, not determined or data is not available.

Jones potential model, the ordinary diffusion coefficient is determined as follows:⁴⁷

$$D(T) = \frac{0.002628T^{1.5}}{(2\mu)^{0.5}\sigma^2 <\Omega^{(1,1)*}(\theta)>}, \text{ atm cm}^2 \text{ s}^{-1} \quad (5)$$

where T is temperature, μ is the reduced mass of the colliding species, $<\Omega^{(1,1)*}(\theta)>$ is the collision integral normalized to its rigid sphere value, $\theta = kT/\epsilon$ is the reduced temperature, and k is Boltzmann's constant. The normalized collision integrals are calculated analytically, and their values are normally tabulated (see, for example, ref 47).

The parameters σ and ϵ of the individual species are required when calculating diffusion coefficients. Normally these parameters are obtained by analysis of the experimental data for second virial coefficients, transport coefficients, and constants characteristic of the critical temperature, melting and boiling points, or by quantum mechanics calculations. These values are known for O_3 (see Table 3a), but there is no such data for OH and HO_2 radicals. In our calculations, we used the σ and ϵ parameters of H_2O to estimate the OH diffusion coefficient and the parameters of H_2O_2 for the HO_2 diffusion coefficient (see Table 3a for a complete list of the parameters for the individual species used in our calculations).^{9,48,49}

Parameters used for calculations of binary diffusion coefficients can be approximated with the parameters of individual species within the Lennard-Jones potential model according to the combination rules:⁴¹

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad \epsilon_{ij} = (\epsilon_i \epsilon_j)^{0.5} \quad (6)$$

Shown in Table 3b is the binary force constants calculated using eq 6. The binary diffusion coefficient describes the ordinary diffusion of a pair of species when only two species are present. However, it is also practical to describe the diffusion coefficient when other species are present.

An estimate of the binary diffusion coefficient in a mixture of several gases can be obtained based on Blanc's law:⁵⁰

$$\frac{1}{D_{\text{mix}}} = \sum_i \frac{\chi_i}{D_i} \quad (7)$$

where χ_i and D_i are the mole fraction and diffusion coefficient of each component of a mixture.

The results of the calculations are compared with the experimental measurements in Table 4. The calculations for OH, HO_2 , and O_3 are in excellent agreement with our measured diffusion coefficients. This provides strong support that this model can be used to predict diffusion coefficients accurately for conditions where no laboratory data exist. For example, this model could be used with high confidence to predict the diffusion coefficient of O_3 in air or HO_2 in air, where measurements have not been performed. Also, the comparison in Table 4 provides stronger support that the diffusion coefficients of OH and HO_2 can be described with high confidence using the collision parameters for the polar analogues.

Our calculations above for OH and HO_2 are similar to the calculations used by Hanson et al. to estimate the diffusion coefficient of OH and HO_2 in a H_2O buffer gas. However, these authors used the diffusion coefficients of O and O_2 (the nonpolar analogues) rather than the polar analogues to represent the diffusion coefficients of OH and HO_2 in a He buffer gas. Our work (both Table 2 and Table 4) shows that a more accurate

TABLE 3: Individual and Calculated Binary Force Constants

| (a) Individual Force Constants | | | |
|-----------------------------------------------|--------------|------------------|-----|
| species | σ , Å | ϵ/k | ref |
| H_2O | 2.641 | 809.1 | 49 |
| H_2O_2 | 4.196 | 298.3 | 9 |
| O_3 | 3.875 | 208.4 | 49 |
| He | 2.556 | 10.22 | 48 |
| N_2 | 3.798 | 71.4 | 49 |
| O_2 | 3.467 | 106.7 | 49 |
| (b) Calculated Binary Force Constants | | | |
| pairs | σ , Å | ϵ/k , K | |
| H_2O –He | 2.596 | 90.93 | |
| H_2O – N_2 | 3.220 | 240.35 | |
| H_2O_2 | 3.054 | 293.82 | |
| H_2O – H_2O | 2.641 | 809.1 | |
| H_2O_2 –He | 3.373 | 55.21 | |
| H_2O_2 – N_2 | 3.997 | 145.94 | |
| H_2O_2 – O_2 | 3.832 | 178.41 | |
| H_2O_2 – H_2O | 3.418 | 491.28 | |
| O_3 –He | 3.086 | 88.489 | |
| O_3 – N_2 | 3.709 | 233.86 | |
| O_3 – O_2 | 3.543 | 285.89 | |
| O_3 – H_2O | 3.131 | 787.26 | |

TABLE 4: Comparison Our Experimental and Calculated (Based on the Polar Analogues for HO_x) Diffusion Coefficients of OH, HO_2 , and O_3 at 1 Torr and 296 K^a

| partner 1 | partner 2 | D_{12} , cm ² s ⁻¹ | |
|---------------|-----------|--------------------------------------------|------------|
| | | measured | calculated |
| OH | He | 662 ± 33 | 636.7 |
| | air | 163 ± 20 | 163.9 |
| HO_2 | He | 430 ± 30 | 407.3 |
| | air | ND | 107.1 |
| O_3 | He | 410 ± 25 | 425.4 |
| | air | ND | 96.3 |

^a ND, not determined or data is not available.

prediction of the diffusion coefficients will result if the polar analogues (H_2O and H_2O_2) are used when predicting the diffusion coefficients in a He buffer gas as well as a H_2O buffer gas. Further studies on the temperature dependence of radical diffusion are needed to verify if the polar analogue approximation is still valid at temperatures different from room temperature.

Conclusions

In the present study, the diffusion coefficients of OH, HO_2 and O_3 in He and OH in air were experimentally measured. On the basis of the obtained results, we conclude that the diffusion of OH and HO_2 is closer to their dipole analogues, namely H_2O and H_2O_2 , rather than to their non-dipole analogues O and O_2 , respectively. The experimental results were also compared with theoretical predictions involving the (6–12) Lennard–Jones potential model. The calculations are in excellent agreement with the experimental measurements, which gives further confidence that these calculations can be used to estimate accurate diffusion coefficients for conditions where no data currently exists. Also the calculations show that diffusion coefficients of OH and HO_2 can be accurately represented using collision parameters of the polar analogues (H_2O and H_2O_2), giving further support that the diffusion of OH and HO_2 can be more accurately represented in the atmosphere by their dipole analogues.

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