Absolute Determination of the Temperature Behavior of the $NO_2 + NO_3 + (M) \leftrightarrow N_2O_5 + (M)$ Equilibrium

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The temperature dependence of the $NO_2 + NO_3 + (M) \leftrightarrow N_2O_5 + (M)$ equilibrium has been studied in the temperature range 279.6−294.2 K at a total pressure of 1000 mbar synthetic air in the 200 m^3 EUPHORE simulation chamber facility in Valencia, Spain. Simultaneous determination of the concentration−time behaviors of NO_3, NO_2, and N_2O_5 were obtained using the DOAS technique for detection of the NO_3 radical and FT-IR spectroscopy for detection of NO_2, and N_2O_5. The experimental data are well described by $\ln([N_2O_5]/[NO_2][NO_3]) = -60.46 \pm 0.26 + (10724 \pm 75)/T$ where the errors given are random and expressed as 95% confidence limits. A critical comparison is made between the values of K_{eq} determined in this work and those reported in the literature.

Introduction

The nitrate radical, NO_3, and its gas-phase chemistry has attracted experimentalists' interest for over 100 years. Since it became evident that the nitrate radical plays a key role in the atmospheric chemistry at night, interest has been focused on investigating its interactions with various other atmospheric constituents. One aspect of this chemistry is the termolecular reaction with nitrogen dioxide and the reverse reaction which together form the equilibrium,

$$NO_2 + NO_3 + (M) \leftrightarrow N_2O_5 + (M) \qquad (1, -1)$$

The temperature dependence of this equilibrium is a critical parameter which is necessary for understanding the NO_x-O_3 chemical system in the nighttime atmosphere. A number of investigations directed toward measuring this equilibrium constant have been reported and include simultaneous measurements of the three species involved and also indirect methods. Reviews concerning the equilibrium (1, −1), henceforth referred to as K_{eq}, can be found in Wayne et al.[1] and in the JPL 97-4 kinetic data compilation.[2] However, inconsistencies exist among the reported equilibrium constants. There are discrepancies between the values obtained using only absolute methods as well as inconsistencies between absolute and indirect determinations of the equilibrium constants.

Here we report the result from an investigation of the temperature dependence on the equilibrium constant performed in a large volume reaction chamber using long-path visible and FT-IR spectroscopy for sensitive and precise simultaneous determination of NO_3, NO_2 and N_2O_5.

Experimental Section

All the equilibrium measurements were performed in one of the two large EUPHORE simulation chambers at the CEAM Institute in Valencia, Spain.[3] This facility consists of two-half-spherical Teflon bags, each with a volume of ≈200 m^3 which are protected against atmospheric influences by two half-sphere-shaped protective metal houses. When closed the metal housing also excludes sunlight from the reactors, thus allowing "dark" chemistry experiments during the day. The concentration−time profiles of NO_2, N_2O_5, and NO_3 were determined simultaneously using in situ long-path FT-IR absorption for measurement of NO_2, and N_2O_5 and long-path differential optical absorption spectroscopy (DOAS) in the visible for measurement of NO_3. The experiments were made at 1002−1015 mbar using purified dry air as the bath gas.

The infrared system consists of a Nicolet, Magna 550 FT-IR spectrometer equipped with an MCT detector which was operated at 1.0 cm^{-1} spectral resolution. The instrument is coupled to a White mirror system (located inside the chamber) with a base length of 8.17 m, see Figure 1. The total optical path length employed was 326.8 m. Spectra were recorded by coadding 115 scans which resulted in a time resolution of 3.2 min per recorded spectrum.

Peak absorbances of NO_2, and N_2O_5 were converted to concentrations using the following cross sections, $\epsilon_{NO_2}(1602\ cm^{-1}, \text{base } 10)^4 = (4.71 \pm 0.26) \times 10^{-19}\ cm^2\ molecule^{-1}$ and $\epsilon_{N_2O_5}(1246\ cm^{-1}, \text{base } 10) = 8.56 \times 10^{-19}\ cm^2\ molecule^{-1}$. The FT-IR cross section of N_2O_5 was calibrated relative to ϵ_{NO_2} using a flow system where NO_2 was converted to N_2O_5 in the presence of excess O_3 according to reaction 2 followed by reaction 1.

$$NO_2 + O_3 \rightarrow NO_3 \qquad (2)$$

The process consisted of passing pure oxygen from a gas flask through a mass flow controller and into a silent discharge ozone generator which produced about 5100 ppm ozone in oxygen at a flow rate of 750 mL min^{-1}. An $NO_2/N_2O_4/N_2$ mixture containing 5−16% NO_2, calculated as $C_{NO_2} = [NO_2] + 2[N_2O_4]$, was passed through a second mass flow controller set to 8−38 mL min^{-1}. The ozone and nitrogen oxide flows were then mixed in a flow reactor (130 cm long, 0.9 cm id, coiled Pyrex tubing) prior to inlet into a 9 cm long FT-IR cell. The absorbances from NO_2 and N_2O_5 were measured at 970 mbar total pressure using a Nicolet 520 FT-IR spectrometer working at 1.0 cm^{-1} resolution. The residence time (6 s) in the Pyrex

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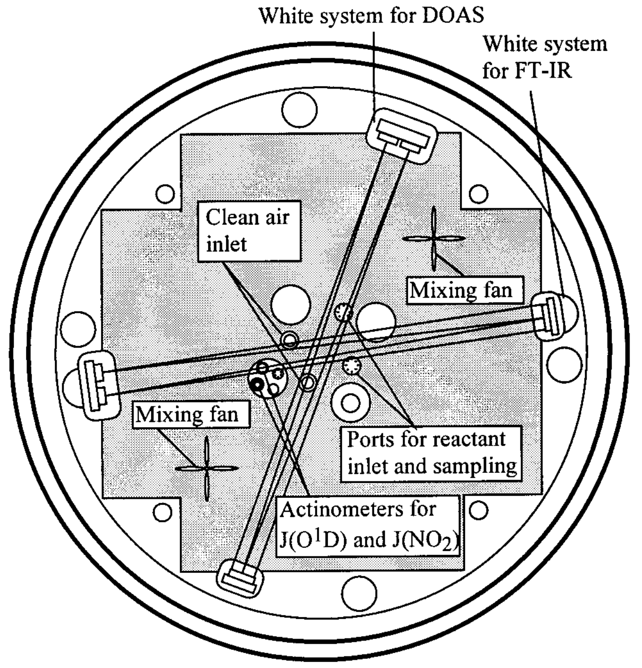

Figure 1. Experimental setup.

reactor was long enough to convert more than 99.9% of all NO_2 to N_2O_5 before the gas entered into the FT-IR cell. With the ozone generator switched off, no O_3 was produced and all NO_2 passed unchanged through the reactor and the total NO_y was measured as NO_2 accompanied by small amounts of N_2O_4. When the ozone generator was switched on, while keeping all gas flows constant, all NO_2 was converted to N_2O_5 and traces of HNO_3. The cross section of N_2O_5 was evaluated assuming a NO_y mass balance according to (I):

$$[N_2O_5] = {}^1/_2[NO_2] + [N_2O_4] - {}^1/_2[HNO_3] \qquad \text{(I)}$$

The cross sections employed for N_2O_4 at 1261 cm^{-1} and HNO_3 at 1326 cm^{-1} were $(1.00 \pm 0.04) \times 10^{-18}$, and $(9.29 \pm 0.4) \times 10^{-19}$ cm^2 $molecule^{-1}$ (base 10), respectively.[4] The first step in each measurement was the determination of the absorbance from NO_2. The ozone generator was then turned on and the absorption from N_2O_5 was measured. On switching off the ozone generator after the measurement the starting NO_2 absorption was obtained, showing that the total NO_y remained constant with time. By varying the initial concentration of NO_2, different N_2O_5 concentrations were obtained.

In addition, data from one experiment in EUPHORE was also used to determine the cross section of N_2O_5 relative to that of NO_2. In one of the equilibrium measurement experiments, the protective housing was opened and N_2O_5 was converted to NO_2 via photolysis of the NO_3 radical. Due to cloudy sky conditions during the day of the experiment it took about 30 min before all the N_2O_5 was destroyed. Assuming the following NO_y mass balance

$$[\mathbf{NO}_y] = [NO_2] + 2[N_2O_5] = \frac{A_{NO_2}}{\epsilon_{NO_2} l} + \frac{2A_{N_2O_5}}{\epsilon_{N_2O_5} l}$$

$$A_{NO_2} = [NO_y]\epsilon_{NO_2} l - \frac{\epsilon_{NO_2}}{\epsilon_{N_2O_5}} 2A_{N_2O_5} \qquad \text{(II)}$$

eq II can be derived where l is the path length and A_{NO_2} and $A_{N_2O_5}$ are the measured infrared absorbances of NO_2 and N_2O_5, respectively. A plot of A_{NO_2} versus $2A_{N_2O_5}$ should yield a straight line with a slope equal to the ratio of the cross-sections of NO_2 and N_2O_5.

The DOAS system has been described in detail elsewhere (Etzkorn et al. in ref 3) and only a brief description will be given here. The analytical light source, a Xe high-pressure arc lamp of 450 W power, was mounted on a platform 2 m underneath the chamber and a Newton-like transfer optics was used to transfer the light to a White multiple reflection system located inside the chamber. The White system (Figure 1) consisted of silver coated mirrors with a focal length of 4 m and a maximum total path length of 1152 m. The light exited the reactor via a second transfer optics which focused the light on a quartz-fiber mode mixer.[5] The end of the quartz fiber is situated just before the entrance slit of a *f*/6.9 Czerny-Turner spectrometer (focal length of 0.5 m, Acton Spectra Pro 500). A 600 g/mm grating with a corresponding dispersion of 0.077 nm/channel was used, resulting in a spectral resolution of 0.42 nm. The spectrometer was thermostated at 30 °C. For recording the spectra a photodiode array detector (Hoffmann-Messtechnik) was used. It is equipped with a Hamamatsu photodiode array (S5931-1024N). The pixel size is 25 μm in width and 2.5 mm in height. To reduce the dark current it was cooled to −25 °C. The photodiode array detector and the spectrometer were controlled by using a software package,[6] developed for this purpose. With this program the measurements could be performed in a completely automatic mode. To reduce the scattered light in the spectrometer and to eliminate higher order radiation from reaching the detector a short-wavelength cutoff filter (OG 590, Schott) was permanently in the light beam.

For the evaluation of NO_3 absorptions a background spectrum, recorded with an interrupted light beam, was subtracted from each sample spectrum. This procedure eliminated effects due to dark current, electronical detector offset and background light. The resulting spectrum was ratioed to a spectrum, recorded just before introduction of NO_3 to the reactor, and logarithmed. The spectrum was then subtracted by its 5000 times triangularly smoothed spectrum. Due to this “mathematical high pass filtering technique” the absorbance in the resulting spectrum is independent of changes in the light intensity and of broad band changes in reflectivity. NO_3 concentrations were calculated using the cross sections of Sander and Kirchner[7] normalized to σ(662 nm, base e) = 2.1×10^{-17} cm^2 $molecules^{-1}$ as recommended by Wayne et al.[1] and assuming a temperature-independent cross section. The NO_3 detection limit obtained was 20 ppt.

The air temperature in the reactor was monitored with a time resolution of 10 s, using five calibrated Pt 100 temperature probes, located at different positions inside the chamber. The temperature of the bulk air could within ±0.2 K be kept uniform, using two strong mixing fans, each having the power of 400 W.

The $N_2O_5/NO_2/NO_3$ mixtures used for the experiments were prepared in much the same way as described above for the N_2O_5 calibration. Here, however, ozone was mixed with NO_2 in excess. The mixing time prior to introduction into the large reactor was long in order to minimize the O_3 concentration. The concentration of O_3 after dilution in the reactor was calculated to be less than 1 ppb and in all experiments it was too low to be detected by FT-IR. By varying the NO_2 flow, different initial $[N_2O_5]/[NO_2]$ ratios could be obtained. Initial $[N_2O_5]/[NO_2]$ ratios were varied from 0.8 to 3.4. During the course of an experiment this ratio decreased slowly with time and more NO_2, or in some experiments, more N_2O_5/NO_2 mixture was added to obtain a broader range. For evaluation of the

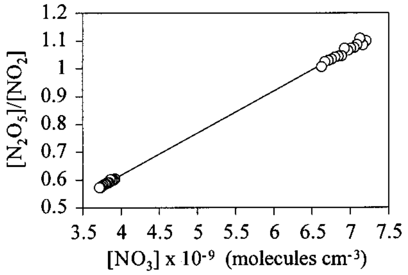

Figure 2. $[N_2O_5]/[NO_2]$ versus $[NO_3]$ from an experiment at 10.4 ± 0.05 °C. Individual equilibrium values form two groups of data as a result of an extra NO_2 addition 48 min after the start of the experiment.

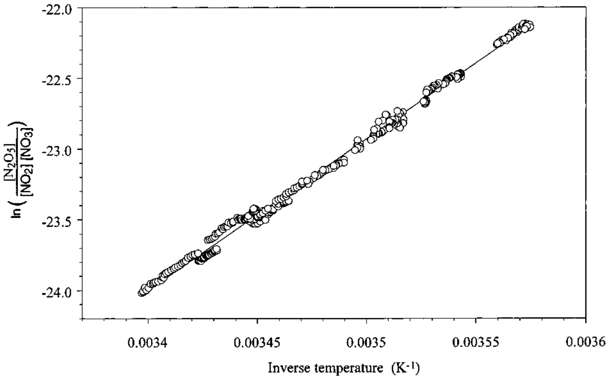

Figure 3. Temperature behavior of the equilibrium $NO_2 + NO_3 \leftrightarrow N_2O_5$ in the range from 279.6 to 294.2 K.

equilibrium constants, the NO_3 concentration versus time was fitted to polynomial functions, from which NO_3 concentrations corresponding to exactly the same time as the NO_2/N_2O_5 data were calculated. Equilibrium constants were then calculated by combining FT-IR and DOAS data applying the expression $K_{eq} = [N_2O_5]/[NO_2]\,[NO_3]$. The concentrations of NO_2, N_2O_5, and NO_3 employed ranged from 72 to 632 ppb, 131 to 573 ppb, and 0.11 to 2.2 ppb, respectively.

Results

The Equilibrium Constant. Ten experiments were done, covering the temperature range from 279.6 to 294.2 K. Each experiment lasted 90−200 min and altogether 353 individual equilibrium constants were determined. All data were fitted to an Arrhenius expression of the form,

$$\ln\left(\frac{[N_2O_5]}{[NO_2][NO_3]}\right) = A + \frac{B}{T} \qquad \text{(III)}$$

where T is the absolute temperature (K) and A and B are the logarithms of the preexponential factor and the $\Delta H/R$ ratio, respectively. The temperature changed during the course of the experiments. In the most extreme case the temperature change was 0.034 deg min^{-1}, but in most experiments the temperature change was less than ±0.009 deg min^{-1}.

In one experiment however, the temperature remained at 10.4 ± 0.05 °C during the 94 min duration of the experiment. The result from this experiment is shown Figure 2, and the equilibrium coefficient, $(1.52 \pm 0.015) \times 10^{-10}$ cm^3 molecule^{-1}, was obtained from the slope of the plot.

The temperature behavior of the equilibrium, $NO_2 + NO_3 \leftrightarrow N_2O_5$, using all the data is shown in Figure 3. The data are well described by eq IV

$$\ln(K_{eq}) = -60.46 \pm 0.26 + (10724 \pm 75)/T \qquad \text{(IV)}$$

where errors given are random and expressed as 95% confidence limits.

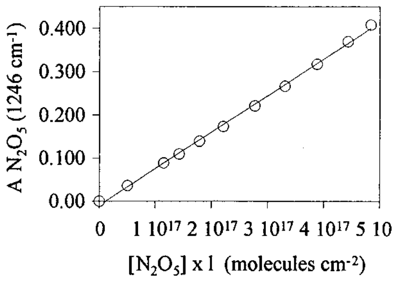

Figure 4. FT-IR calibration of N_2O_5 according to eq I.

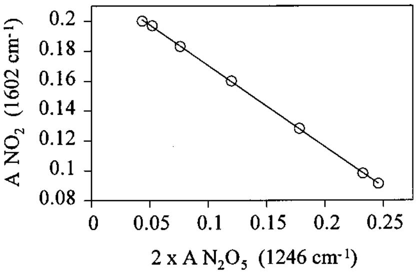

Figure 5. Ratio of NO_2 and N_2O_5 FT-IR cross sections according to eq II.

FT-IR Calibration of N_2O_5. In Figure 4, the absorbance of N_2O_5 at 1246 cm^{-1} is plotted versus $[N_2O_5]l$, where $[N_2O_5]$ is calculated according to eq I and l is the optical path length. The data yields a straight line, whose slope is equal to $\epsilon_{N_2O_5}$(1246.6 cm^{-1}, base 10) = $(8.45 \pm 0.24) \times 10^{-19}$ cm^2 molecule^{-1}. The stated error is expressed as 95% confidence limits. This cross section is based on a ϵ_{NO_2}(1602 cm^{-1}, base 10) value[4] equal to $(4.71 \pm 0.26) \times 10^{-19}$ cm^2 molecule^{-1}. The result from the photolysis experiment is presented in Figure 5. A cross-section ratio of 0.543 ± 0.008 was obtained, which in combination with the ϵ-value of NO_2 at 1602 cm^{-1} yields $\epsilon_{N_2O_5}$ (1246.6 cm^{-1}, base 10) = $(8.67 \pm 0.13) \times 10^{-19}$ cm^2 molecule^{-1}. The errors given are random and expressed as 95% confidence limits

Discussion

Previous absolute K_{eq} determinations are compared with the results from this study in Table 1. Since the results determined in this study are only valid in the temperature range from 279.6 to 294.2 K the value given for $K_{eq}(298)$ was obtained by extrapolation. As can be seen the present value at 298 K is close to the measurements made by Burrows et al.[8] and that of Perner et al.,[9] but differs significantly from the values reported by Cantrell et al.,[11] and Hjorth et al.[12] A comparison of the Arrhenius plots from the various studies, shown in Figure 6, again highlights the agreement between the present work and that of Burrows et al.[8] It has been shown[12] that the slightly different spectroscopic parameters employed in the earlier measurements can only partially explain the disagreements between the different studies; i.e., the discrepancies between the reported equilibrium constants are larger than the differences in the spectroscopic parameters used in these determinations. Although the N_2O_5 cross section employed here is slightly higher than in previous determinations, the large difference between the present result and some previous reports can also not be rationalized in terms of using different spectroscopic parameters.

Among the previous absolute measurements, the work by Cantrell et al.[11] is probably the most thorough and it is also the study with the most extensive temperature range. It can be noted that the temperature dependence, i.e., the value for the $\Delta H/R$ ratio, obtained in this work is very close to that obtained by

TABLE 1: Summary of Results from Temperature-Dependent Studies on the Equilibrium $NO_2 + NO_3 \leftrightarrow N_2O$[a]

temp range (K)	A (cm^3 molecule^{-1})	$B \pm \Delta B$ (K)	K_{eq}(298 K) × 10^{11} (cm^3 molecule^{-1})	reference[b]
297.4−298.8			3.44×10^{-11}	Tuazon et al.,[10] 1984 (a)
275.0−315.0	8.10×10^{-29}	11958 ± 1018	2.17×10^{-11}	Burrows et al.,[8] 1985 (a)
298.2−300.4			2.15×10^{-11}	Perner et al.,[9] 1985 (a)
242.8−397.0	7.69×10^{-27}	10818 ± 216	4.48×10^{-11}	Cantrell et al.,[11] 1988 (a)
293.0−298.0	4.50×10^{-26}	10226 ± 2180	3.73×10^{-11}	Hjorth et al.,[12] 1992 (a)
200.0−300.0	2.7×10^{-27}	11000 ± 500	2.90×10^{-11}	Cantrell et al.,[13] 1993 (r)
200.0−300.0	2.46×10^{-27}	11028	2.90×10^{-11}	J. Phys. Chem. Ref. Data,[14] 1997 (e)
200.0−300.0	2.7×10^{-27}	11000 ± 500	2.90×10^{-11}	JPL Publication 97-4,[2] (e)
279.6−294.2	5.50×10^{-27}	10724 ± 75	2.34×10^{-11}	this work (a)

[a] The information is given in the form $K_{Eq}(T) = A \exp((B \pm \Delta B))/T)$, where T is the absolute temperature (K), A is the Arrhenius factor, and $B \pm \Delta B$ is the temperature dependence and associated uncertainty. [b] a, r, and e denote absolute measurements, relative measurement, and evaluations, respectively.

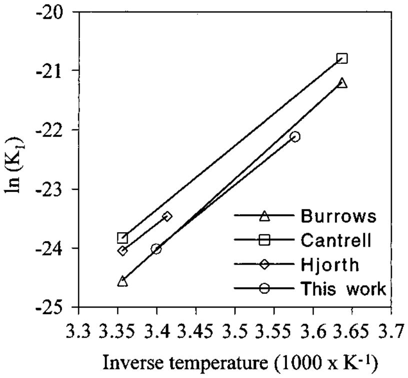

Figure 6. Arrhenius plots, showing $\ln(K_{eq})$ in the range 275−298 K. Only part of the temperature range investigated by Burrows et al.[8] and Cantrell et al.[11] are shown in the Figure.

Cantrell et al.[11] However, on closer inspection of the Arrhenius expression from this study, eq IV, and that of Cantrell et al.,[11] eq V,

$$\ln(K_{eq}) = -60.13 \pm 0.66 + (10818 \pm 216)/T \qquad \text{(V)}$$

where the errors given are also expressed as 95% confidence limits, it can be seen that although the associated uncertainty range in the ln A factor and in the $\Delta H/R$ ratio of Cantrell et al.[11] embraces the corresponding values measured in this work the reverse is not true; i.e., the $\ln(K_{eq})$ values of Cantrell et al.[11] lie outside the uncertainty range of the $\ln(K_{eq})$ values measured in this work.

Although the K_{eq} values obtained in this work have been measured with a good statistical precision, the accuracy in terms of possible systematic errors needs to be discussed. A summary of infrared cross-sections of NO_2 and N_2O_5 has been reported.[15] The difference between different measurements of the infrared cross section of the 1600 cm^{-1} band of NO_2 is only ± 2%; thus this property seems to be well established. Concerning N_2O_5, differences among the measurements are as large as 35%, probably reflecting difficulties involved in quantitatively handling this sticky and reactive gas. The infrared cross section of N_2O_5 at 1246.6 cm^{-1} was determined in two different experiments using a mass-balance assumption as previously mentioned. One uncertainty regarding the experiment where N_2O_5 was produced by reacting NO_2 with excess O_3 was that the system also contained N_2O_4 and HNO_3. The concentrations of these gases were accounted for in the mass balance by measuring their absorptions, and thus, giving an uncertainty due to the possible uncertainty in their infrared cross sections. The concentrations of N_2O_4 and HNO_3 were, however, low and thus, the maximum contribution of these gases to the total NO_y was only 3% and 1%, respectively. The contribution from N_2O_4 and HNO_3 can therefore be regarded as negligible.

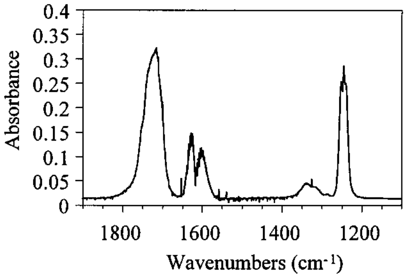

Figure 7. FT-IR spectrum showing NO_2 (at 1600 cm^{-1}) and N_2O_5 (at 1246 and 1720 cm^{-1}). A small absorption at 1326 cm^{-1}, due to HNO_3, can also be seen. Water has been subtracted from the spectrum.

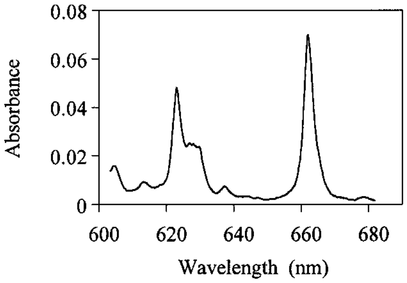

Figure 8. Absorbance spectrum of NO_3, corresponding to 2.9×10^{10} molecules cm^{-3}. The spectrum is not high-pass filtered.

The photolysis experiment in the EUPHORE reactor yielded a cross section which is identical, within the limits of error, with that determined using the flow reactor and, therefore, the value $\epsilon_{N_2O_5}$(1246.6 cm^{-1}, base 10) = $(8.56 \pm 0.53) \times 10^{-19}$ cm^2 molecule^{-1}, which corresponds to the average of the two measurements was chosen. In the stated error for the $\epsilon_{N_2O_5}$ value, the error in the cross section of NO_2 is also included.

The accuracy with which NO_2 and N_2O_5 can be measured is also dependent on the quality of the FT-IR spectra. One critical aspect of the measurements of the NO_2 absorbance is the influence from water bands. The NO_2 analysis was, however, improved by first subtracting the water bands followed by using the NO_2 rotational band at 1602 cm^{-1}, where the intensity from water is at minimum. With this procedure the influence from water on the measurements was almost eliminated. Figure 7 shows a FT-IR spectrum after subtraction of water.

Since $\epsilon_{N_2O_5}$ was derived experimentally as a direct multiple of ϵ_{NO_2} any systematic error in the NO_2 cross section would be canceled out when calculating the $[N_2O_5]/[NO_2]$ ratio. The accuracy with which the $[N_2O_5]/[NO_2]$ ratio could be measured was estimated to ±5% which includes errors in the cross-section ratio and in the absorbance measurements.

The DOAS measurements yielded NO_3 spectra of very high quality. Figure 8 shows an NO_3 absorbance spectrum measured in the beginning of one experiment. Concerning the absorptivity of NO_3, there is reasonable agreement in the literature on the absorption cross-section values at 298 K; recent measurements agree to within ±10% on the value of the cross section at 662 nm.[1] Although uncertainties exist regarding the temperature dependence of the absorption cross section at 662 nm, the cross section appears to increase slightly with decreasing temperature. The following average temperature-dependent cross section at 662 nm was deduced using the average values from several investigations:[1] $\sigma(662\ \text{nm}) = (3.63 - (5.13 \times 10^{-3}T)) \times 10^{-17}$ $\text{cm}^2\ \text{molecule}^{-1}$. When using this expression to calculate NO_3 cross sections for the temperature range investigated here, the difference between the highest value at 279.6 K and that of 294.2 K is only 3.5%. The most recent measurements of the cross section of NO_3 have been performed by Yokelson et al.[16] They determined a cross section of $\sigma(662\ \text{nm, base e}) = 2.23 \times 10^{-17}\ \text{cm}^2\ \text{molecule}^{-1}$ at 298 K and a temperature dependence which is described by the expression $\sigma(662\ \text{nm}) = (4.56 - (7.87 \times 10^{-3}T)) \times 10^{-17}\ \text{cm}^2\ \text{molecule}^{-1}$. This temperature dependence is higher and corresponds to an increase of about 5% when going from 294.2 to 279.6 K. The temperature dependence of the NO_3 absorption cross section, thus, seems to be somewhat uncertain. Since, for the present temperature interval, the overall uncertainty in the NO_3 cross section appears to be greater than the variation with temperature, NO_3 concentrations for all temperatures were calculated using the value $\sigma_{NO_3}(298\ \text{K, 662 nm, base e}) = 2.1 \times 10^{-17}$, as recommended by Wayne et al.,[1] which corresponds to the average of several investigations.[7,17-19] Other equilibrium values, based on another choice of NO_3 cross section may, however, be calculated by multiplying our K_{eq} expression, $5.50 \times 10^{-27} \exp[10724/T]$, by $\sigma(T)/2.1 \times 10^{-17}$, where $\sigma(T)$ is a NO_3 absorption cross section of one's own choice.

From the above discussion we believe that the present measurements are reliable and recommend the following equilibrium constant for use in the temperature range from 279.6 to 294.2 K

$$K_{eq} = 5.50 \times 10^{-27} \exp[10724/T] \qquad \text{(VI)}$$

Based on a propagation of errors calculation including uncertainties in the measurements of the $[N_2O_5]/[NO_2]$ ratio and the NO_3 concentration, the overall accuracy is estimated to be ±15%.

As mentioned above, K_{eq} values calculated from eq VI fall in the lower end of the range of literature data obtained from absolute measurements. The value at 298 K is very close to those from Burrows et al.[8] and Perner et al.[9] Burrows et al.[8] used a lower NO_3 cross section than in this study; if their K_{eq}(298 K) value is recalculated using the higher NO_3 cross section from this work, a value of $2.35 \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ is obtained, in excellent agreement with this study. Recent indirect measurements also suggest lower values for K_{eq}. Cantrell et al.,[13] for example, calculated the temperature dependence of K_{eq} using the pressure and temperature dependence of the rate coefficient for reaction 1, reported by Orlando et al.,[20] and the rate coefficient for reaction −1.[13] The result is given in Table 1 and yields a K_{eq}(298 K) value of $2.90 \times 10^{-11}\ \text{cm}^{-3}\ \text{molecule}^{-1}$, which is 24% higher than the present equilibrium constant. Our result may also be compared to the equation obtained from a similar calculation, taking $k_1([N_2], T)$ and $k_{-1}([N_2], T)$ rate coefficients from a recent critical evaluation of kinetic data (*J. Phys. Chem. Ref. Data* **1997**).[14] The result from this calculation is shown in Table 1.

Although the present $NO_2 + NO_3 \leftrightarrow N_2O_5$ equilibrium measurements cover a limited temperature range, the result is interesting as it covers common tropospheric summer night temperatures corresponding to mid and northern latitudes. Since, the equilibrium partly controls the NO_3 radical concentrations, lower values mean higher tropospheric NO_3 concentrations than previously believed. This implies that NO_3 may be more important in initiating oxidizing processes in the atmosphere. N_2O_5 should, on the other hand, be less important as a reservoir of NO_3 radicals, thereby making heterogeneous conversion of N_2O_5 to HNO_3 on wet particles slightly less important.

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References and Notes

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