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Rate Constants of the Reactions of $O(^3P)$ Atoms with Br_2 and NO_2 over the Temperature Range 220 – 950 K

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ABSTRACT: The kinetics of the reactions of Br_2 and NO_2 with ground state oxygen atoms have been studied over a wide temperature range, T = 220 – 950 K, using a low pressure flow tube reactor coupled with a quadrupole mass spectrometer: $O + NO_2 \rightarrow NO + O_2$ (1) and $O + Br_2 \rightarrow Br + BrO$ (2). The rate constant of reaction (1) was determined under pseudo-first order conditions, either monitoring the kinetics of O-atom or NO_2 consumption in excess of NO_2 or of the oxygen atoms, respectively: $k_1 = (6.1 \pm 0.4)\times10^{-12} \exp((155 \pm 18)/T)$ $cm^3molecule^{-1}s^{-1}$ (where the uncertainties represent precision at the 2σ level, the estimated total uncertainty on k_1 being 15% at all temperatures). The temperature dependence of k_1, found to be in excellent agreement with multiple previous low temperature data, was extended to 950K. The rate constant of reaction (2) determined under pseudo-first order conditions, monitoring the kinetics of Br_2 consumption in excess of O-atoms, showed upward curvature at low and high temperatures of the study and was fitted with the following three-parameter expression: $k_2 = 9.85\times10^{-16}\ T^{1.41} \exp(543/T)$ $cm^3molecule^{-1}s^{-1}$ at T = (220 – 950) K, which is recommended from the present study with an independent of temperature conservative uncertainty of 15% on k_2.

Keywords: Oxygen atom, Br_2, NO_2, rate coefficient, temperature dependence.

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Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

INTRODUCTION

The reaction of ground state atomic oxygen with nitrogen dioxide is of great atmospheric importance as a rate limiting step in catalytic cycle destroying odd oxygen ($O+O_3$) in the middle stratosphere and affecting both the abundance and vertical profile of the stratospheric ozone [1]:

$$O+NO_2 \rightarrow NO + O_2 \qquad (1)$$

Besides the atmospheric importance, the reaction is often used in laboratory studies as a titration reaction of oxygen atoms and is included in NO_2 sub-mechanism of kinetic models for combustion systems [2]. Hence, it is not surprising that kinetics of the reaction (1) has been studied very extensively in the past [3-14]. Currently, the rate constant of the $O+NO_2$ reaction, k_1, can be considered as well established in the temperature range T = 220 – 425K [15]. At higher temperatures only three studies of the reaction are available [5,8,11]. However, the most extended measurements of k_1 over the temperature range T = 297 – 1055K reported by Bemand *et al*. [8] are highly scattered and do not match the extrapolation of the Arrhenius expression for k_1 based on the low temperature data [15]. In addition, the reaction rate constant at high temperatures has been recently challenged by appearance of a theoretical study [16], predicting U-shaped temperature dependence of k_1 with rapid increase of the rate constant with temperature at T > 400 K. In this respect, the objective of the present work was to extend the measurements of k_1 to high temperatures in order to compare them with previous experimental data and new theoretical predictions.

The reaction of oxygen atoms with Br_2 was studied as a part of this work:

$$O+Br_2 \rightarrow Br + BrO \qquad (2)$$

In fact, this reaction was used for detection of low concentrations of oxygen atoms *via* their chemical conversion to BrO radicals [17]. However, it is also of autonomous interest. Although this reaction is not of direct atmospheric importance, it is very often used in the laboratory as a source of BrO radicals, which is an important species in the atmospheric bromine/ozone chemistry [18]. The rate constant of the reaction (2), k_2, especially its temperature dependence, is highly uncertain. Thus, in four previous temperature dependent kinetic studies of the reaction [19-22], noticeable positive [19,20] and negative [22] dependence of k_2 on temperature as well as independent of temperature k_2 [21] were reported. In the present work, we have performed measurements of the reaction rate constant in an extended temperature range T = 220 – 950 K.

EXPERIMENTAL

The rate constants of the title reactions were measured at total pressure of ≈ 2 Torr of He in a discharge flow reactor combined with a modulated molecular beam mass spectrometer [17,23,24]. Two flow reactors were used. The first one, used at low temperatures (T = 220 – 317 K), consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (ethanol). The inner surface of the reactor as well as of the movable injector of O atoms was coated with halocarbon wax (HW) in order to minimize their heterogeneous loss. The second flow reactor, operating at high temperatures (T = 294 – 950 K), consisted of an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled extremities (Fig. 1S, Supporting Information) [25]. Kinetic measurements were carried out in the part of the reactor where temperature gradient along the reaction zone (measured with a thermocouple inserted in the reactor through the movable injector [25]) was less than 1% (Fig. 1S, Supporting Information).

Oxygen atoms were generated from the microwave discharge in O_2/He mixtures. Two methods were used for the detection of oxygen atoms. At high concentrations of O atoms (experiments in excess of O atoms over Br_2 or NO_2), they were detected at their parent peak at m/z=16 (O^+). The absolute concentrations of the atoms were determined from the fraction of O_2 dissociated in the microwave discharge ($\Delta[O_2] = 2[O]$). At low concentrations of oxygen atoms (experiments in excess of NO_2 over oxygen atoms), another method for their detection was preferred to the direct one at m/z = 16 due to significant residual signal at this mass. Br_2 was added at the end of the reactor (6 cm upstream of the sampling cone, Fig. 1S) in order to transform O atoms to BrO detected at m/z=95/97 as BrO^+:

$$O + Br_2 \rightarrow BrO + Br \qquad (2)$$

$k_2 = 9.85\times10^{-16}\ T^{1.41} \exp(543/T)$ cm^{3}molecule^{-1}s^{-1} (T = 220-950 K, this work).

The concentrations of Br_2 (~ 10^{14} molecule cm^{-3}) were high enough to ensure rapid consumption of oxygen atoms. The impact of the recombination reaction of BrO radicals (3) and reaction (4) of BrO with NO (product of reaction (1)) on the measurements of [BrO] was insignificant due to relatively low concentrations of these species (initial concentration of oxygen atoms was ≤ 4×10^{11} molecule cm^{-3}):

$$BrO + BrO \rightarrow \text{products} \qquad (3)$$

$k_3 = 1.5\times10^{-12} \exp(230/T)$ cm^{3}molecule^{-1}s^{-1} over T = 220-348 K [15].

$$BrO + NO \rightarrow Br + NO_2 \qquad (4)$$

$k_4 = 8.8\times10^{-12}\ \exp(260/T)$ cm^{3}molecule^{-1}s^{-1} over T = 224-425K [15].

Reaction of BrO witn NO_2 was also slow under experimental conditions of the study:

$$BrO + NO_2\ (+M) \rightarrow BrONO_2\ (+M) \quad (5)$$

$k_5 < 2.3\times10^{-13}$ cm^{3}molecule^{-1}s^{-1} at $T \geq 220$K and P = 2 Torr [15].

Absolute concentrations of BrO radicals were determined using their chemical conversion to NO_2 through reaction (4) in excess of NO with subsequent detection of NO_2 formed ($[BrO]_0 = [NO_2]_{formed}$). For stable species ($NO_2$, NO, Br_2, O_2), the mass spectrometer was calibrated by introducing their known concentrations into the reactor from their calibrated mixtures with helium. The uncertainty on the absolute concentrations of the stable species was ≤ 10%. All species were detected by mass spectrometry at their parent peaks: m/z= 46 (NO_2^+), 30 (NO^+), 158/160/162 (Br_2^+), 95/97 (BrO^+), 32 (O_2^+), 16 (O^+).

RESULTS AND DISCUSSION

Reaction O + NO_2

Measurements of k_1. The reaction rate constant was determined under pseudo-first order conditions either from kinetics of O-atom consumption ($[O]_0 \leq 4\times10^{11}$ molecule cm^{-3}) in excess of NO_2 or from NO_2 decays ($[NO_2]_0 \leq 5\times10^{11}$ molecule cm^{-3}) monitored in excess of oxygen atoms. The ranges of concentrations of the respective excess reactants are shown in Table I. The flow velocity in the reactor was in the range (1950-2300) cm s^{-1}. The concentrations of O and NO_2 were simultaneously measured as a function of reaction time. Generally, the consumption of excess reactant was negligible (within a few percent), although reaching up to 25 % in a few kinetic runs at lowest concentrations of the excess reactant: in all cases the average concentration of excess reactant along the reaction zone was used in calculation of the reaction rate constant. This simplified procedure did not significantly affect the calculated rate constants, which could also be derived from the simulation of the experimental NO_2 (or O-atom) kinetics using the observed temporal profiles of excess reactant. The values of k_1 obtained by the two methods were in agreement within 4%.

Examples of O-atom and NO_2 decays observed at different concentrations of NO_2 and oxygen atoms, respectively, are shown in Figs. 1 and 2S (Supporting Information).

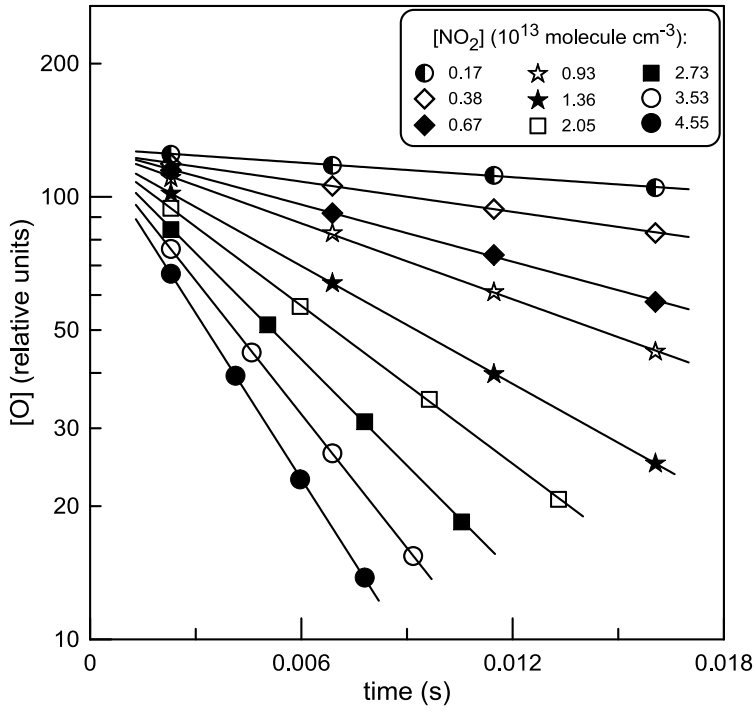

Figure 1 Reaction O + NO_2: example of the exponential decays of O atoms in excess of NO_2 at T = 950 K.

The pseudo-first order rate constants, $k_1' = k_1[NO_2] + k_w$, determined from the slopes of the straight lines, like those in Figs. 1 and 2S, are shown in Fig. 2 as a function of NO_2 concentration. The intercepts in Fig. 2, k_w, were in the range (1 - 9) s^{-1}, in good agreement with the rate of O-atom decay measured in separate experiments in the absence of NO_2 in the reactor. Diffusion corrections were applied to all the measured values of k_1' in order to take into account the axial and radial gradient of O-atom concentration in the flow tube: $k_1' = k_{1\,measured}' \times (1 + k_{1\,measured}' \times D/v^2 + k_{1\,measured}' \times r^2/48D)$, where D is the molecular diffusion coefficient, v is the flow velocity and r is the radius of the flow tube [26]. The diffusion coefficient of O in He was calculated using D_0 = 770 Torr cm^2 s^{-1} at T = 298K [27] and assuming $T^{1.75}$-dependence on temperature. Corrections were generally less than 9 %, and only in three kinetic runs at T = 950 K they were somewhat higher, up to 16%. Examples of the dependence of pseudo-first order rate constant $k_1' = k_1[O]$ measured from NO_2 decays on concentration of excess reactant, oxygen atom, are shown in Fig. 3. Diffusion corrections on k_1' calculated in this case using the diffusion coefficient of NO_2 in He, $D_0 = 550\times(T/298)^{1.75}$ Torr cm^2 s^{-1} (estimated with Fuller's method) [28], were less than 8%.

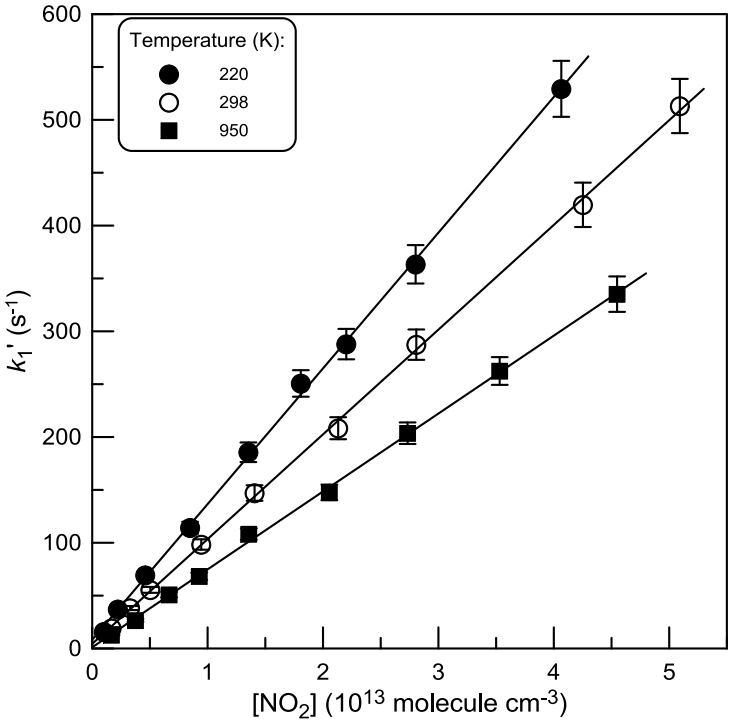

Figure 2 Reaction O + NO_2: dependences of pseudo-first order rate constant of O-atom decay on concentration of NO_2 measured at T = 220, 298 and 950 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.

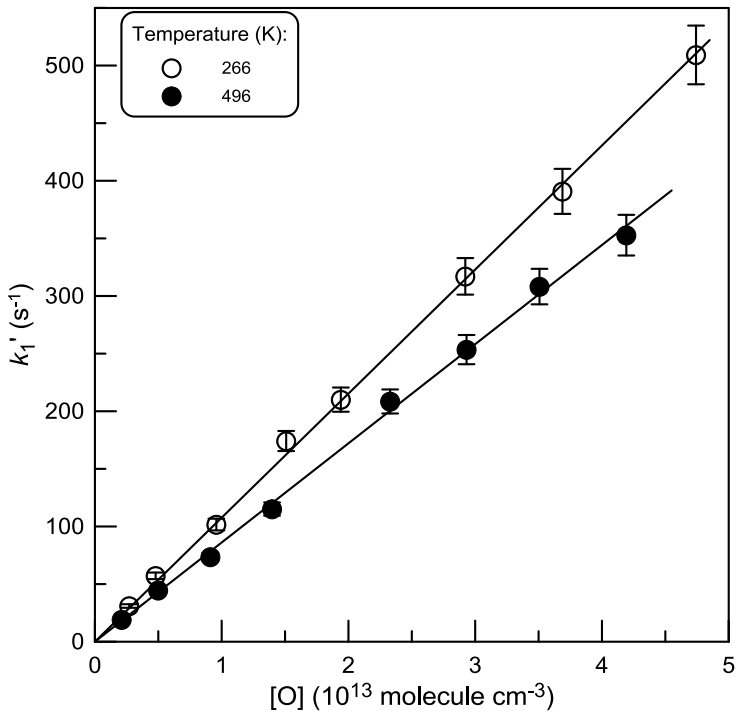

Figure 3 Reaction O + NO_2: dependences of pseudo-first order rate constant of NO_2 decay on concentration of oxygen atoms measured at T = 266 and 950 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.

The slopes of the straight lines in Figs. 2 and 3 provide the values of k_1 at respective temperatures. All the results obtained for k_1 in the present study are shown in Table I and Fig.

4. One can note very good agreement between the values for k_1 obtained from kinetics of O-atom and NO_2 consumption. The combined uncertainty on the measurements of k_1 was estimated to be of nearly 15 %, by adding in quadrature (square root of the sum of squares) the statistical error (≤ 4 %) and those on the measurements of the flows (5%), pressure (2%), temperature (1%), and absolute concentrations (10%) of NO_2 and oxygen atoms.

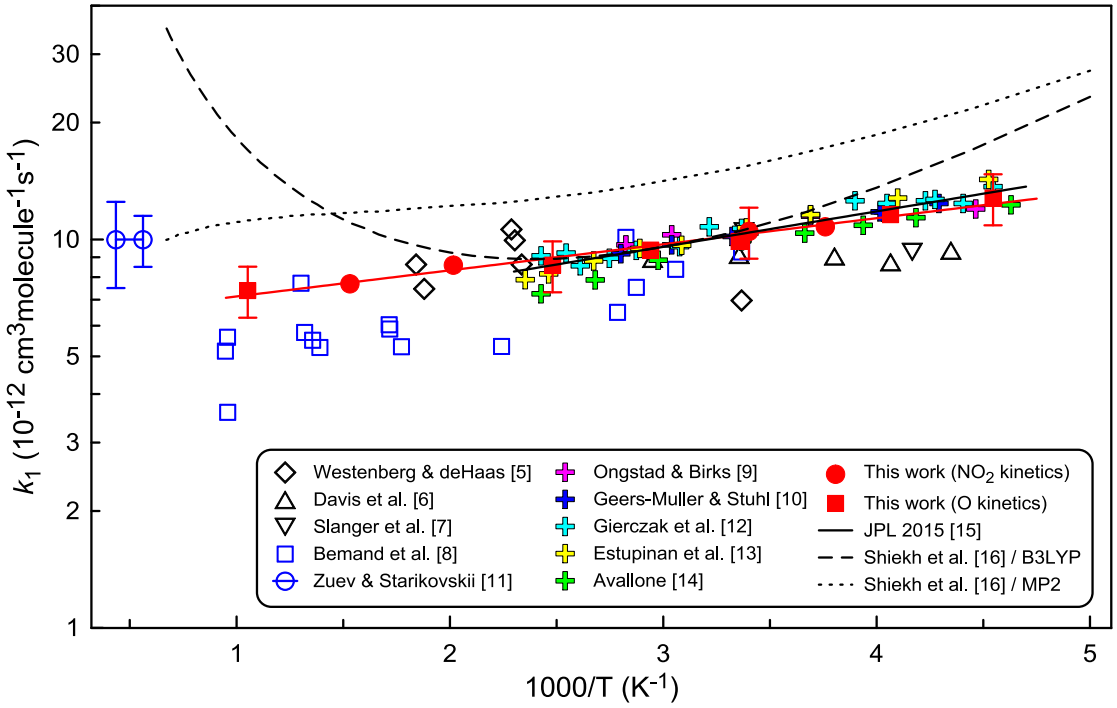

Figure 4 Reaction O + NO_2: summary of the measurements of the temperature dependence of the reaction rate constant. Error bars correspond to estimated 15 % uncertainty on the measurements of k_1 in the present work. Uncertainties on k_1 reported in previous studies are omitted for clarity.

Comparison with previous data. Figure 4 summarizes the results of temperature dependent measurements [5-14] of the rate constant of reaction (1). Westenberg and deHaas [5] have measured the reaction rate constant at T = 297-543 K in a fast-flow reactor combined with electron spin resonance (ESR) spectroscopy. Davis *et al*. [6], using flash photolysis-resonance fluorescence technique have reported temperature independent k_1 = (9.12 ± 0.44)×10^{-12} cm^{3}molecule^{-1}s^{-1} over the temperature range T = 230-339 K. Close results were obtained by Slanger *et al*. [7] who measured k_1 = 9.3 and 10.5×10^{-12} cm^{3}molecule^{-1}s^{-1} and T = 296 and 240K, respectively, using pulsed photolysis and the O +NO + M chemiluminescent emission for detection of O-atoms. In the only high temperature study of reaction (1), using atomic resonance fluorescence, Bemand *et al*. [8] measured k_1 at 16 temperatures between 298 and 1055 K (average values of k_1 at each temperature are shown in Fig. 4) and observed a slight negative temperature dependence of the rate constant. Small negative activation factor (E_a/R) of the reaction (1) has been confirmed in all subsequent work: 142 ± 23 K over the

temperature range 220-387 K, in a discharge flow study with chemiluminescent detection of O-atoms [9]; 202 ± 27 K over T = 199-357 K, using flash photolysis with chemiluminescent reaction of O-atoms with NO [10]; 209 ± 35 K over T = 220-412 K, using pulsed laser photolysis of NO_2 to produce oxygen atoms and time-resolved vacuum UV resonance fluorescence for their detection [12]; 273 ± 18 K over T = 221-425 K, with laser flash photolysis-resonance fluorescence technique [13] and 165 ± 10 K over T = 216-413 K by discharge-flow resonance fluorescence technique [14]. The Arrhenius expression recommended by the JPL panel (black continuous line in Fig. 4) [15], $k_1 = 5.1\times10^{-12}$ exp(210/T) cm^{3}molecule^{-1}s^{-1}, is based on the measurements reported in refs. [7,9,10,12,13]. A least-squares fit to k_1 data from the present work (red line in Fig. 4) provides the following Arrhenius expression:

$$k_1 = (6.1 \pm 0.4)\times10^{-12} \exp((155 \pm 18)/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

over the temperature range 220-950 K and with 2σ statistical uncertainties on the fit. Although this expression is somewhat different from recommended by JPL panel [15], the absolute values of k_1 measured in the present study are in excellent agreement with the most recent measurements [9,10,12-14] of the rate constant and current recommendation [15] at $T \leq$ 425 K. At higher temperatures, present values of k_1 are higher than those reported by Bemand *et al*. [8] by a factor of 1.3-1.9. One can also note that possible downward curvature of the Arrhenius plot at temperatures above 298 K discussed in ref. [14] is not confirmed by the present measurements.

In a recent theoretical study, the rate constant of the reaction (1) was computed over a temperature range 150–1500 K [16]. The values of k_1 calculated at two different levels of theory (B3LYP/aug-cc-pVTZ and MP2/6-311+G(d,p)) are shown in Fig. 4. The authors concluded that computed values of k_1 are in "an excellent agreement (within 5–10%) with all the available experimental data particularly at B3LYP method". As one can see from Fig. 4, this statement is valid only in a rather narrow temperature range. In fact, the temperature dependence of k_1 predicted by simulations at the B3LYP level of theory does not reproduce the experimental results. Shiekh *et al*. [16] noted that the nonlinear behavior of k_1 calculated with B3LYP method at higher temperatures may be due to the limitations of VPT2 model in this temperature range. On the other hand, the calculations with MP2 method seem to better reproduce temperature dependence of k_1 although they are shifted by a factor of 1.4-1.7 with respect to the experimental data. Zuev and Starikovskii [11] in their shock tube study of thermal decomposition of N_2O reported $k_1 = (1.0 \pm 0.25)\times10^{-11}$cm^{3}molecule^{-1}s^{-1} at T = 1780-

2300 K. This value was derived from an analysis of concentration profiles of N_2O, NO_2 and NO within a complex kinetic mechanism including nine reversible reactions. Although the indirect measurement of k_1 [11] is by a factor of ≈ 1.5 higher than the extrapolation of the present data to these temperatures, the results from two studies are consistent in the range of reported uncertainties. On the other hand, our experimental data on k_1 measured at $T \leq 950$K do not exclude the possible upward curvature in the temperature dependence of k_1 at higher temperatures.

Reaction O + Br_2

Measurements of k_2. The rate constant of the reaction O+Br_2 was measured under pseudo-first order conditions from kinetics of Br_2 consumption ($[Br]_0 \leq 3\times10^{11}$ molecule cm^{-3}) in excess of oxygen atoms. The concentrations of O-atoms at different temperatures of the study are shown in Table II, the flow velocity in the reactor was in the range (2315-3000) cm s^{-1}.

Typical example of Br_2 decays observed with different excess concentrations of oxygen atoms in the reactor is shown in Fig. 3S (Supporting Information). Figures 5 and 4S (Supporting Information) present examples of the pseudo-first order rate constant, $k_2' = k_2[O]$, as a function of concentration of oxygen atoms. The values of k_2' were corrected for axial and radial diffusion [26] of Br_2. The diffusion coefficient of Br_2 in He, $D_0 = 276\times(T/298)^{1.75}$ Torr cm^2 s^{-1}, used in the calculations was estimated with Fuller's method [28]. Corrections on k_2' were generally less than 10 % and reached up to 24% at lowest temperatures of the study. The slopes of the straight lines in Figs. 5 and 4S provide the values of k_2 at respective temperatures. All the values of k_2 measured in the present work are shown in Table II and Fig. 6.

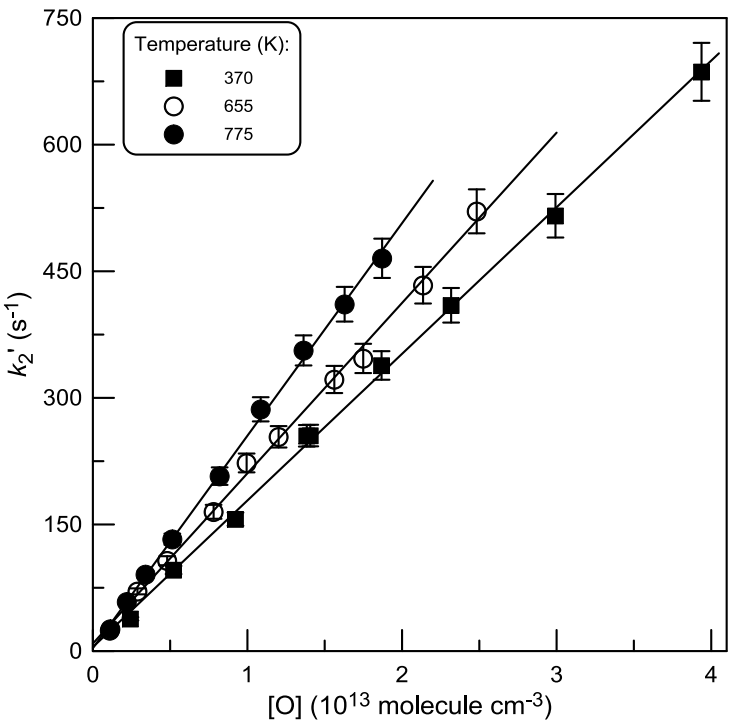

Figure 5 Reaction O + Br_2: dependences of pseudo-first order rate constant of Br_2 consumption on concentration of oxygen atoms measured at T = 370, 655 and 775 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.

Comparison with Previous Data. The results of the present measurements of k_2 are shown in Fig. 6 together with those from previous studies [19-22,29]. Clyne *et al*. [29] using atomic resonance fluorescence determined the rate constant of reaction (2) in a discharge flow system both from the rate of removal of O-atom in excess of Br_2 and from the rate of formation of Br in excess of oxygen atoms over Br_2: $k_2 = (1.4 \pm 0.2)\times10^{-11}$ cm^{3}molecule^{-1}s^{-1} at T = 298 K. Moin *et al*. [19] measured the rate constant of reaction (2) relative to that of O-atom reaction with Cl_2, $k_2/k_6 = 3.98 \times \exp(1310/T)$ at T = (306 – 425) K (uncertainty factor of 3.4), using diffusion flame method combined with electron paramagnetic resonance detection of oxygen atoms:

$$O + Cl_2 \rightarrow ClO + Cl \qquad (6)$$

With $k_6 = 7.4\times10^{-12} \exp(-1650/T)$ cm^{3}molecule^{-1}s^{-1} [30], the reported by Moin *et al*. [19] k_2/k_6 ratio leads to $k_2 = 2.95\times10^{-11} \exp(-340/T)$ cm^{3}molecule^{-1}s^{-1}. These data, being highly uncertain and not suitable for quantitative comparison, are shown in Fig. 6 for completeness. Dodonov *et al*. [20], have also used diffusion flame method to measure the rate constant of reaction (2) over the temperature range 246-431 K: $k_2 = 4.6\times10^{-11} \exp(-(210\pm75)/T)$ cm^{3}molecule^{-1}s^{-1}. Nicovich and Wine [21] employed laser flash photolysis-resonance fluorescence technique to measure the rate constant of reaction (2) and found virtually independent of temperature k_2 =

$(1.76 \pm 0.8)\times10^{-11}\exp((40 \pm 100)/T)$ cm^{3}molecule^{-1}s^{-1} in the temperature range 255 – 350 K. The rate constant data reported by Nicovich and Wine [21] are in excellent agreement with those of the present work.

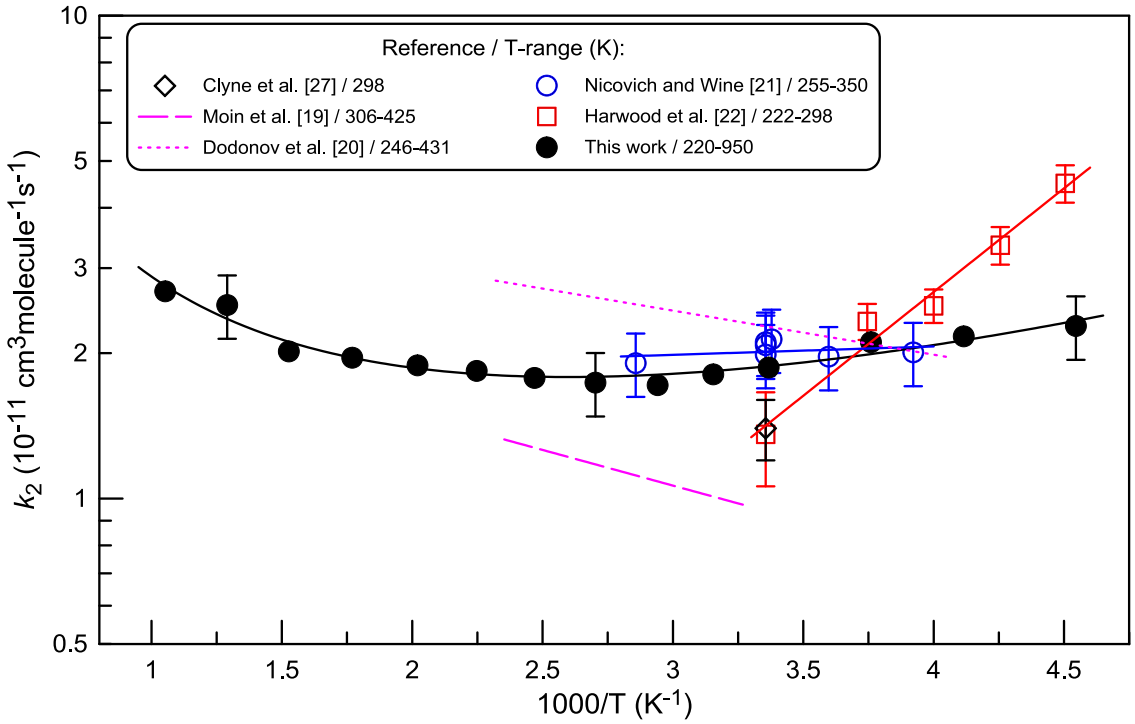

Figure 6 Reaction O + Br_2: summary of the measurements of the reaction rate constant. Error bars represent the uncertainties reported in the respective studies: estimated total uncertainty of 15% in Nicovich and Wine [21] and present work; 1σ statistical uncertainty in Harwood *et al*. [22].

Finally, in a most recent study [22], the rate constant for the reaction of oxygen atoms with molecular bromine was determined in an indirect way from the measurements of [BrO] to [O_3] ratio upon photolysis of O_2 in the presence of Br_2: $k_2 = (5.12 \pm 1.86)\times10^{-11}\exp((989 \pm 91)/T)$ cm^{3}molecule^{-1}s^{-1} at T = 222 – 298 K:

$$O + Br_2 \rightarrow BrO + Br \qquad (2)$$

$$O + O_2\,(+M) \rightarrow O_3\,(+M) \qquad (7)$$

One can note that at low temperatures the values of k_2 measured in the present work differ considerably (up to a factor of 2 at T = 220 K) from those reported by Harwood *et al*. [22]. Three-parameter fit to the present data for k_2 provides the following expression for the rate constant of the O+Br_2 reaction:

$$k_2 = 9.85\times10^{-16}\,T^{1.41}\exp(543/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \text{ at } T = (220 – 950)\ \text{K},$$

which is recommended from the present study with an independent of temperature conservative uncertainty of 15% on k_2. The information on the rate constant at elevated

temperatures may be useful for the future kinetic studies related to high-temperature bromine chemistry in near-vent volcanic plumes [31].

Both negative and U-shaped temperature dependence observed for reactions of oxygen atoms with NO_2 and Br_2, respectively, indicate a complex mechanism of these reactions. In this respect, further theoretical high level calculations in comparison with the experimental observations would be very beneficial to understand the dynamics of the processes in these relatively simple chemical systems.

CONCLUSION

In this work, using two (low and high temperature) flow reactors, we have measured the rate constants of the reactions of $O(^3P)$ atoms with NO_2 and Br_2 over an extended temperature range, 220 – 950 K. The temperature dependence of the rate constant of the important atmospheric reaction of oxygen atoms with NO_2, found to be in excellent agreement with multiple previous data at $T \leq 425$ K, was extended to $T = 950$K. Both negative and U-shaped temperature dependence of the rate constant observed for reactions of oxygen atoms with NO_2 and Br_2, respectively, seem to represent an interesting experimental basis for further theoretical developments. The high temperature data on the rate constant of the O + Br_2 reaction may be useful for the laboratory kinetic studies related to high-temperature bromine chemistry in volcanic plumes.

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TABLE LEGENDS

Table I Reaction $O + NO_2 \rightarrow NO + O_2$: Experimental Conditions and Results of the Measurements of the Reaction Rate Constant

Table II Reaction $O + Br_2 \rightarrow Br + BrO$: Experimental Conditions and Results of the Measurements of the Reaction Rate Constant

FIGURE LEGENDS

Figure 1 Reaction O + NO_2: example of the exponential decays of O atoms in excess of NO_2 at T = 950 K.

Figure 2 Reaction O + NO_2: dependences of pseudo-first order rate constant of O-atom decay on concentration of NO_2 measured at T = 220, 298 and 950 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.

Figure 3 Reaction O + NO_2: dependences of pseudo-first order rate constant of NO_2 decay on concentration of oxygen atoms measured at T = 266 and 950 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.

Figure 4 Reaction O + NO_2: summary of the measurements of the temperature dependence of the reaction rate constant. Error bars correspond to estimated 15 % uncertainty on the measurements of k_1 in the present work. Uncertainties on k_1 reported in previous studies are omitted for clarity.

Figure 5 Reaction O + Br_2: dependences of pseudo-first order rate constant of Br_2 consumption on concentration of oxygen atoms measured at T = 370, 655 and 775 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.

Figure 6 Reaction O + Br_2: summary of the measurements of the reaction rate constant. Error bars represent the uncertainties reported in the respective studies: estimated total uncertainty of 15% in Nicovich and Wine [21] and present work; 1σ statistical uncertainty in Harwood *et al*. [22].

TABLES

Table I Reaction O + NO_2 → NO + O_2: Experimental Conditions and Results of the Measurements of the Reaction Rate Constant

T (K)	[Excess reactant] (10^{13} molecule cm^{-3}) [a]	k_1 (10^{-11} cm^3 $molecule^{-1}$ s^{-1}) [b]
220	0.10-4.07	1.28 ± 0.03
246	0.28-4.47	1.16 ± 0.02
266	0.27-4.74	1.08 ± 0.02
294	0.10-4.37	1.05 ± 0.04
298	0.17-5.09	0.99 ± 0.02
340	0.27-4.40	0.94 ± 0.02
403	0.35-4.50	0.86 ± 0.02
496	0.21-4.19	0.86 ± 0.03
653	0.18-3.23	0.77 ± 0.03
950	0.17-4.55	0.74 ± 0.02

[a] excess reactant: oxygen atom at T = 266, 294, 496 and 653 K, NO_2 at all other temperatures
[b] the errors correspond to 2σ statistical uncertainty

Table II Reaction O + Br_2 → Br + BrO: Experimental Conditions and Results of the Measurements of the Reaction Rate Constant

T (K)	[O] (10^{13} molecule cm^{-3})	k_2 (10^{-11} cm^3 $molecule^{-1}$ s^{-1}) [a]
220	0.23-2.83	2.28 ± 0.08
243	0.16-3.21	2.17 ± 0.06
266	0.14-2.42	2.11 ± 0.04
297	0.11-2.73	1.87 ± 0.06
317	0.22-3.08	1.81 ± 0.04
340	0.26-3.16	1.72 ± 0.08
370	0.24-3.94	1.74 ± 0.06
405	0.16-3.05	1.78 ± 0.04
445	0.21-2.88	1.84 ± 0.10
495	0.06-1.56	1.89 ± 0.06
565	0.11-2.96	1.96 ± 0.10
655	0.11-2.48	2.02 ± 0.08
775	0.11-1.87	2.52 ± 0.08
950	0.16-1.96	2.69 ± 0.22

[a] the errors correspond to 2σ statistical uncertainty

Supporting Information

Rate Constants of the Reactions of $O(^3P)$ Atoms with Br_2 and NO_2 over the Temperature Range 220 – 950 K.

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Number of pages (including this one): 3
Number of Figures: 4

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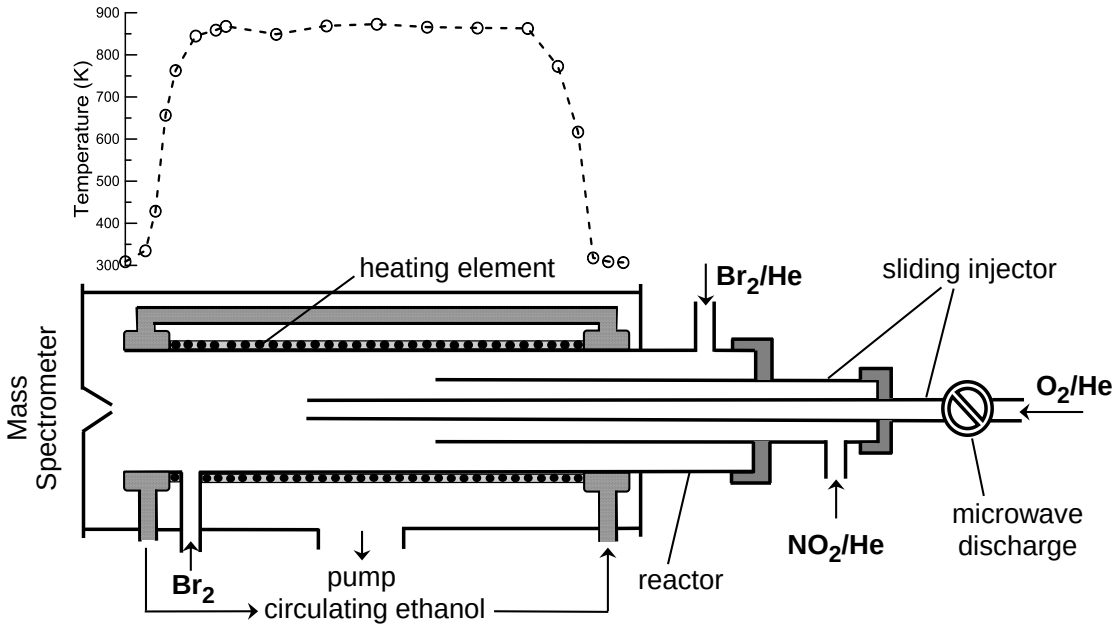

Figure 1S Diagram of the flow reactor.

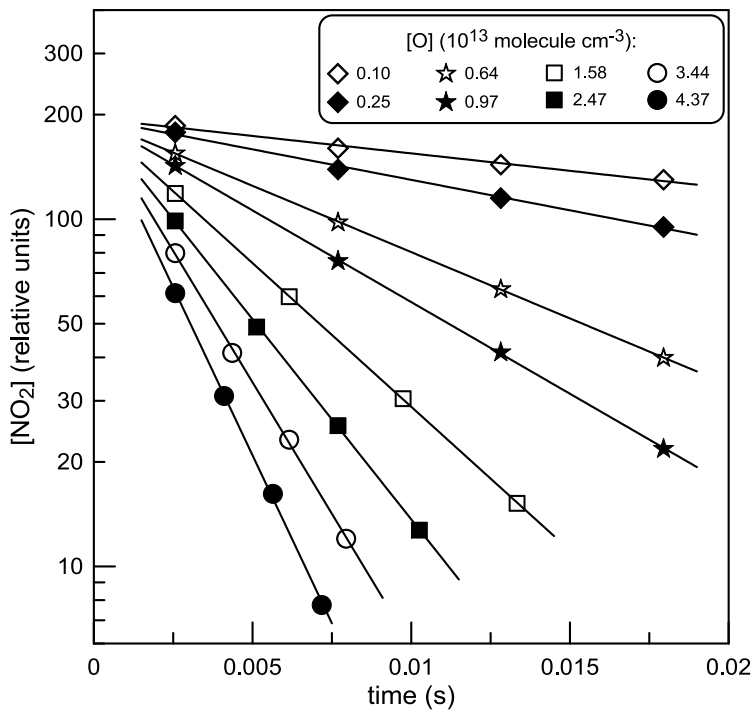

Figure 2S Reaction O + NO_2: example of the exponential decays of NO_2 in excess of oxygen atoms at T = 294 K.

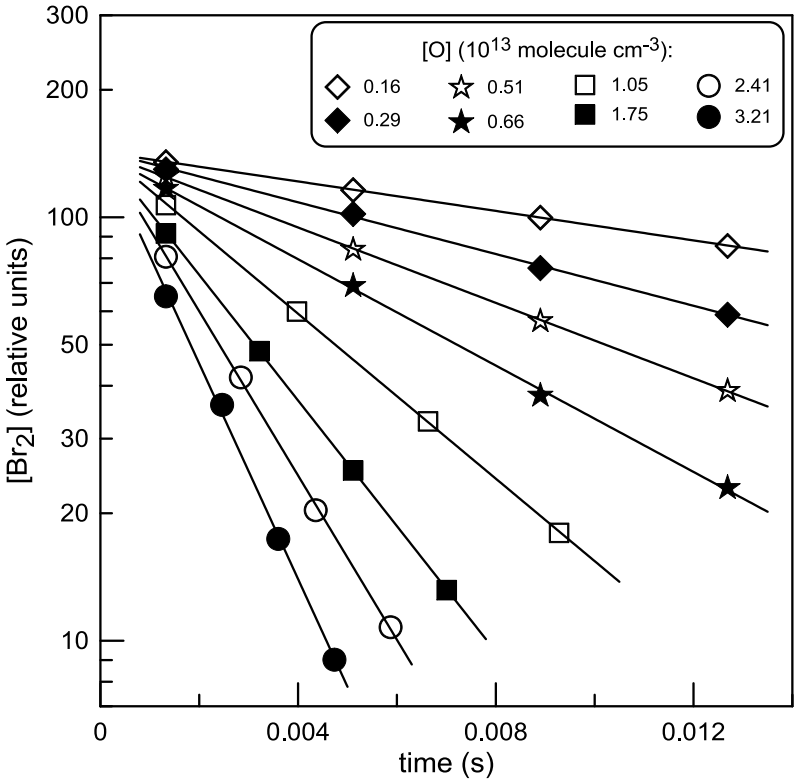

Figure 3S Reaction O + Br_2: example of the exponential decays of Br_2 in excess of oxygen atoms at T = 243 K.

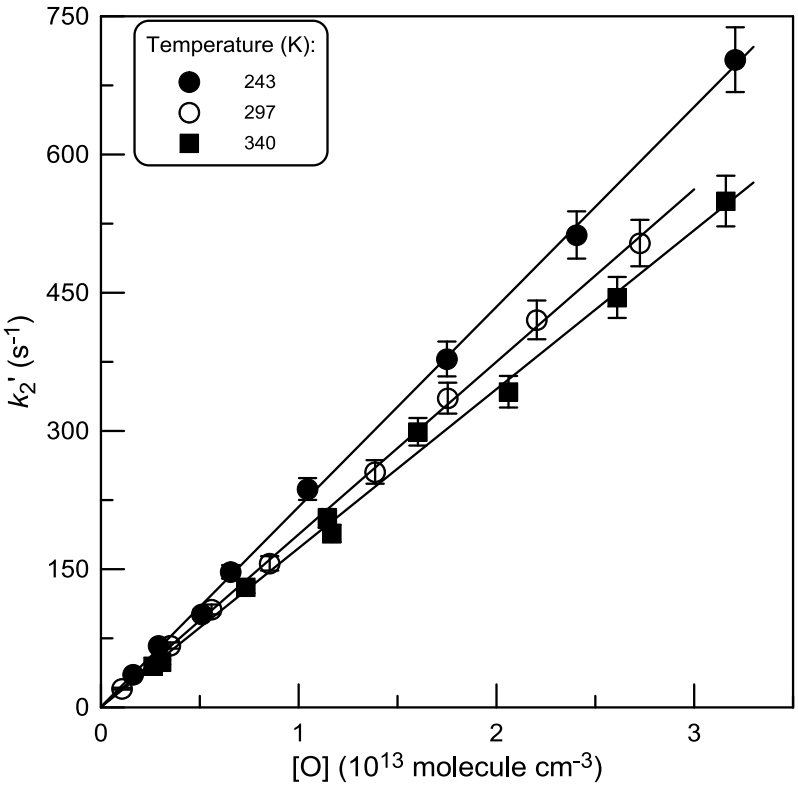

Figure 4S Reaction O + Br_2: dependences of pseudo-first order rate constant of Br_2 consumption on concentration of oxygen atoms measured at T = 243, 297 and 340 K. Error bars represent maximum uncertainty of nearly 5 % on determination of k_1'.