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Rate Constant of the Reaction of OH radicals with HBr over the Temperature Range 235–960 K

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ABSTRACT

The kinetics of the reaction of hydroxyl radical with HBr, important in atmospheric and combustion chemistry, has been studied in a discharge flow reactor combined with an electron impact ionization quadrupole mass spectrometer in the temperature range 235 – 960 K. The rate constant of the reaction OH + HBr $\rightarrow$ H_2O + Br (1) was determined using both relative rate method (using reaction of OH with Br_2 as a reference) and absolute measurements, monitoring the kinetics of OH consumption under pseudo-first order conditions in excess of HBr. The observed U-shaped temperature dependence of k_1 is well represented by the sum of two exponential functions: $k_1 = 2.53\times10^{-11}\exp(-364/T) + 2.79\times10^{-13}\exp(784/T)$ $cm^3molecule^{-1}s^{-1}$ (with estimated conservative uncertainty of 15% at all temperatures). This expression for k_1 recommended for T = 240-960 K combined with that from previous low temperature studies, $k_1 = 1.06\times10^{-11}(T/298)^{-0.9}$ $cm^3molecule^{-1}s^{-1}$ at T = 23-240 K, allows to describe the temperature behavior of the rate constant over an extended temperature range 23-960 K. The current direct measurements of k_1 at temperatures above 500 K, the only ones to date, provide an experimental dataset for use in combustion and volcanic plume modelling and an experimental basis to test theoretical calculations.

1. INTRODUCTION

Reaction of OH radicals with HBr

$$OH + HBr \rightarrow H_2O + Br \qquad (1)$$

is an important atmospheric reaction playing a central role in bromine partitioning between its active forms and reservoirs through transformation of the reservoir species HBr to Br-atom.[1] Reaction (1) has been extensively studied, both experimentally and theoretically, over the past decades. Currently, for the temperature range 230-360 K, there is a consensus on the slight negative temperature dependence and on the absolute value of the reaction rate constant (k_1).[2-5] Kinetic studies carried out at ultra-low temperatures (down to 23 K), although somewhat scattered, have revealed a strong inverse temperature dependence of k_1 below 200 K.[6-10]

Reaction (1) is also important in combustion chemistry being an important step in flame inhibition mechanisms when using bromine-containing compounds as flame-retardants.[11-13] Another potential implication of the reaction at high temperatures is its involvement in the hot near-source volcanic plume chemistry.[14] Surprisingly, despite the potential practical interest in the reaction at high temperatures, there are no experimental data for the reaction rate constant at temperatures higher than 460 K. Recent theoretical work on the OH + HBr reaction was also mainly focused on temperatures below 500 K,[refs] and only a few evaluations[11] and theoretical efforts[15-16] have been undertaken to define the reaction rate constant at elevated temperatures. Although all these works predict a similar small positive temperature dependence of k_1 at T > 500 K, the absolute values of k_1 differ by more than a factor of 2.

The objective of the present study consisted in the measurements of the rate constant of reaction (1) in the temperature range extended to ca. 1000 K in order to provide new experimental data for combustion modelling and validation of the theoretical calculations.

2. EXPERIMENTAL

Kinetic measurements have been conducted at nearly 2 Torr total pressure of Helium using a conventional fast-flow reactor combined with a molecular beam sampling electron-impact ionization mass spectrometer operated at 25–30 eV energy.[17-19] Two different flow reactors were used depending on the temperature of the measurements. High temperature reactor, used at T = 320 – 960 K, consisted of an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled attachments (Figure S1a, Supporting Information (SI)).[19] Low temperature reactor (Figure S1b, SI), used at T = 235 – 325 K, consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) surrounded by a jacket through which a thermostated ethanol was circulated. The internal surface of the low temperature reactor was coated with Halocarbon wax in order to reduce the heterogeneous loss of OH radicals.

OH radicals were produced inside the movable injector in a rapid reaction of hydrogen atoms with excess NO_2 ($[NO_2] = (1.0\text{-}1.5)\times10^{13}$ molecule cm^{-3}):

$$H + NO_2 \rightarrow OH + NO \qquad (2)$$

$k_2 = (1.47 \pm 0.26) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (T = 195 – 2000).[20]

H atoms, in turn, were generated from the microwave discharge in highly diluted H_2/He mixtures (Figures S1a and S1b). Prior to their sampling to the mass spectrometer, hydroxyl radicals were converted to HOBr in the fast reaction with Br_2 ($[Br_2] = (4 - 6)\times10^{13}$ molecule cm^{-3}, added in the end of the reactor 6 cm upstream of the sampling cone as shown in Figure S1b),

$$OH + Br_2 \rightarrow HOBr + Br \qquad (3)$$

$k_3 = 2.16\times10^{-11} \exp(207/T)$ $cm^3 molecule^{-1} s^{-1}$ (T = 220 – 950),[18]

and were finally detected at m/z = 96/98 ($HOBr^+$). Reaction (3) in excess of Br_2 was also used for the determination of the absolute concentrations of OH radicals by linking [OH] to the consumed fraction of $[Br_2]$: $[OH] = [HOBr] = \Delta[Br_2]$.[21-22]

HBr was transported to the reactor by flow of the bath gas (He) over HBr solution in water. The absolute calibration of the mass spectrometer for HBr was realized using chemical conversion of H-atom to HBr in reaction with excess Br_2:

$$H + Br_2 \rightarrow HBr + Br \quad (4)$$

In this way, the concentration of HBr formed in reaction (4) was related to the fraction of Br_2 consumed. The absolute concentrations of other stable species (H_2, NO_2, Br_2) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop in their manometrically prepared mixtures with He stored in calibrated volume flasks. All species were detected by mass spectrometry at their parent peaks: m/z= 160 (Br_2^+), 96/98 ($HOBr^+$), 46 (NO_2^+), 80/82 (HBr^+).

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap; H_2 > 99.998% (Alphagaz); Br_2 >99.99% (Aldrich); NO_2 > 99% (Alphagaz); HBr, 48 wt. % in H_2O > 99.99% (Sigma-Aldrich). The concentration of Br_2 impurity in HBr, measured by mass spectrometry, was less than 0.1%.

3. RESULTS AND DISCUSSION

3.1. Absolute Measurements of k_1. The absolute measurements of k_1 were carried out under pseudo-first order conditions monitoring consumption of hydroxyl radicals ($[OH]_0$ = (1 - 3)×10^{11} molecule cm^{-3}) in excess of HBr (the ranges of the initial concentrations of HBr used are shown in Table 1).

Table 1. Summary of the absolute measurements of k_1

T (K) [a]	[HBr] (10^{13} molecule cm^{-3})	k_1 (± 2σ) (10^{-11} cm^3 $molecule^{-1}$ s^{-1})	Reactor surface [b]
235	0.25-4.60	1.31±0.03	HW
250	0.30-4.08	1.23±0.02	HW
265	0.34-4.78	1.21±0.02	HW
280	0.32-4.06	1.17±0.03	HW
300	0.29-4.55	1.10±0.02	HW

320	0.19-3.12	1.14±0.02	Q
325	0.21-4.69	1.08±0.02	HW
370	0.14-4.48	1.18±0.02	Q
410	0.24-2.00	1.26±0.02	Q
450	0.10-3.03	1.27±0.02	Q
500	0.11-2.24	1.38±0.02	Q
540	0.11-2.15	1.43±0.02	Q
620	0.09-1.43	1.51±0.03	Q
650	0.07-2.56	1.52±0.03	Q
700	0.10-2.51	1.58±0.02	Q
760	0.06-1.65	1.63±0.02	Q
800	0.07-2.11	1.61±0.02	Q
880	0.12-2.72	1.73±0.02	Q
960	0.05-1.61	1.82±0.03	Q

[a] 8-13 kinetic runs at each temperature. [b] HW: halocarbon wax; Q: Quartz.

The flow velocity in the reactor was in the range (1750-2920) cm s^{-1}. The kinetics of OH consumption in excess of HBr were treated with an exponential function, $[OH] = [OH]_0 \times \exp(-k_1' \times t)$, where $k_1' = k_1 \times [HBr] + k_w$ is the pseudo-first-order rate constant and k_w corresponds to the rate of OH loss on the walls of the flow reactor. Examples of the kinetic runs observed at T = 700 K are shown in Figure S2 (SI). Examples of the typical dependencies of the pseudo-first order rate constant, $k_1' = k_1 \times [HBr] + k_w$, on concentration of HBr at different temperatures are shown in Figure 1. The consumption of the excess reactant, HBr, monitored by mass spectrometry, was observed to be less than 10% in all the kinetic runs. In all cases, the average concentration of HBr along the reaction zone was used in the treatment of the experimental data. All measured values of k_1' were corrected for the effects of axial and radial diffusion of OH radicals.[23] Typically, the corrections were <10 % and up to 18% in a few kinetic runs. The values of k_1 at respective temperatures were determined from the slopes of the straight lines like those shown in Figure 1.

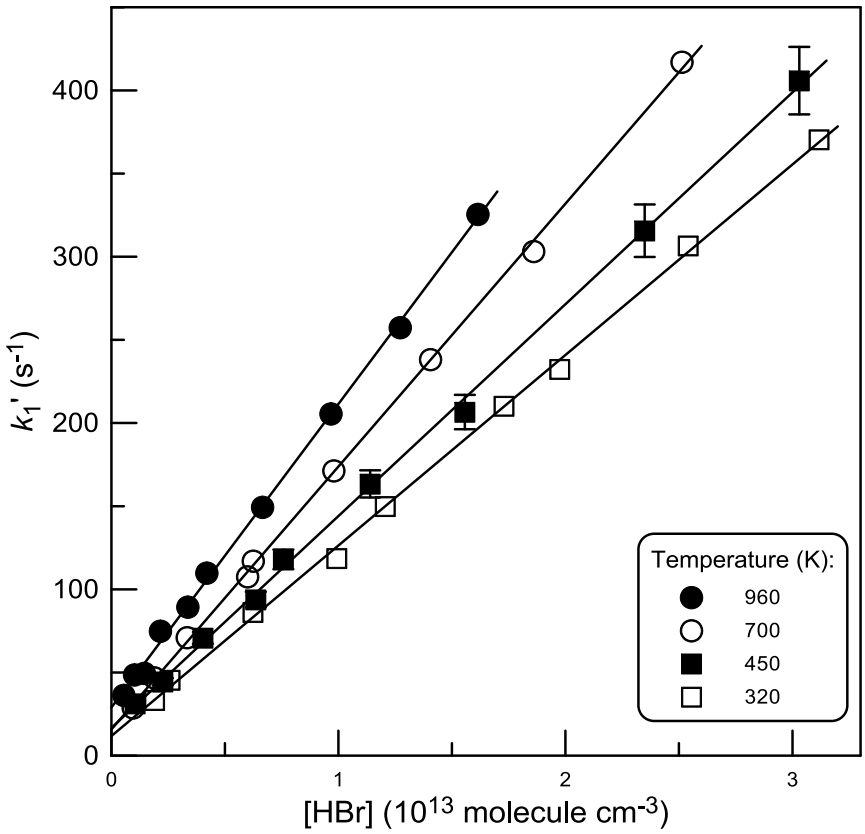

Figure 1. Plots of pseudo-first-order rate constant k_1' versus concentration of HBr at different temperatures. Partially shown error bars represent typical uncertainties (≤5%) on the determination of k_1'.

All the results of the absolute measurements of k_1 at different temperatures are shown in Table 1. The combined uncertainty on the measurements of the rate constants was estimated to be of nearly 15 %, including (in quadrature) statistical error (within a few percent, Table 1) and those on the measurements of the flows (5%), pressure (3%), temperature (1%) and absolute concentration of HBr (≤ 10%).

3.2. Relative Measurements of k_1. In this series of experiments, the rate constant of reaction (1) was measured relative to that of OH radicals with Br_2. The experiments consisted in a titration of hydroxyl radicals by a mixture of HBr and Br_2 and the measurements of HOBr yield as a function of the [HBr]/[Br_2] ratio:

$$OH + HBr \rightarrow H_2O + Br \quad (1)$$

$$OH + Br_2 \rightarrow HOBr + Br \quad (3)$$

The fraction of the initial concentration of OH radicals, $[OH]_0$, transformed to HOBr in reaction 3, is:

$$[\mathrm{HOBr}] = \frac{k_3[\mathrm{Br_2}]}{k_3[\mathrm{Br_2}]+k_1[\mathrm{HBr}]+k_w} \times [\mathrm{OH}]_0$$

Rearrangement of this expression provides:

$$\frac{[\mathrm{OH}]_0}{[\mathrm{HOBr}]} - 1 = \frac{k_1[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]} + \frac{k_w}{k_3[\mathrm{Br_2}]} \qquad \text{(I)}$$

At a constant concentration of Br_2, the second term in equation (I) is constant and k_1/k_3 can be determined as a slope of the linear dependence of ($[OH]_0$/[HOBr] - 1) on the [HBr]/[Br_2] ratio. The measurements of the absolute concentrations of OH were not necessary in these experiments, since HOBr was monitored in the presence of Br_2 in both HBr -free system, corresponding to $[OH]_0$, and in the presence of HBr in the reactor, corresponding to the fraction of $[OH]_0$ reacted with Br_2. Reaction time was around 0.02 s, $[OH]_0 = (0.5\text{-}1.0)\times10^{11}$, $[Br_2] \approx 9\times10^{12}$ molecule cm^{-3}, the ranges of HBr concentrations are given in Table 2.

Table 2. Experimental Conditions and Results of the Relative Measurements of k_1

T (K)	[HBr] [a]	[HBr]/[Br_2]	k_1/k_3 (± 2σ)	k_1 [b]
340	0.40-12.5	0.36-11.1	0.289±0.004	1.15
510	0.37-7.00	0.36-6.20	0.421±0.005	1.36
730	0.25-8.37	0.24-6.91	0.573±0.005	1.64
920	0.23-7.69	0.21-5.90	0.663±0.007	1.79

[a] Units of 10^{13} molecule cm^{-3}. [b] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, estimated total uncertainty on k_1 is nearly 20% and includes the uncertainty on the rate constant of the reference reaction.

The experimental data observed in relative measurements of k_1 are shown in Figure 2. In accordance with Equation I, the slopes of the straight lines in Figure 2 provide the values of k_1/k_3 at respective temperatures. Final values of k_1 (Table 2) were calculated with $k_3 = 2.16\times10^{-11}\exp(207/T)$ $cm^3molecule^{-1}s^{-1}$, recommended in a recent study from this group in the temperature range T = 220-950 K.[18]

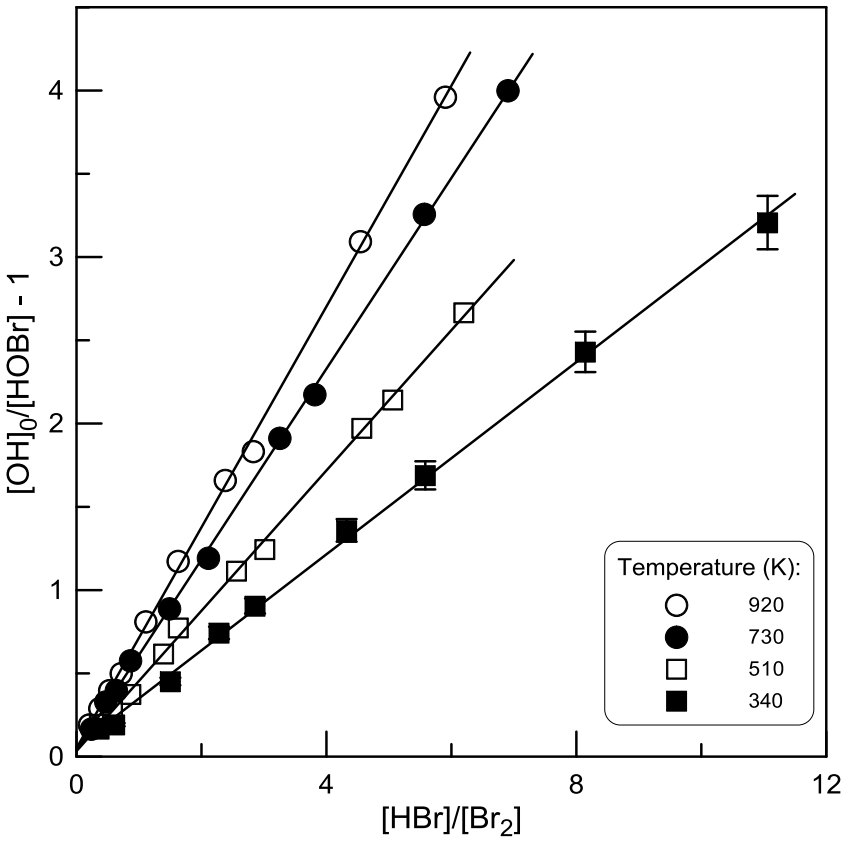

Figure 2. Yield of HOBr from titration of OH radicals by Br_2 + HBr mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (~ 5%).

3.3. Comparison with Previous Data. Figure 3 summarizes the results of the present measurements of k_1 in comparison with those from three previous temperature dependence studies realized in overlapping temperature ranges.[3,5,24] Concerning the results from this study, one can note an excellent agreement between absolute and relative measurements of the reaction rate constant. In the range of the reported uncertainties on the measurements of k_1, the current data (T=235-960 K) match very well those from previous study from this group (T=230-360 K),[3] as well as the laser flash photolysis-resonance fluorescence measurements of Ravishankara et al. (T=249-416 K)[5] and recently reported results of discharge flow-electron paramagnetic resonance study by Khamaganov et al. (T = 298, 370 and 460 K).[24] Three most recent room temperature measurements of the reaction rate constant (reporting the values of k_1 between 0.92 and 1.12×10^{-11} $cm^3molecule^{-1}s^{-1}$),[25-27] in turn, are in good agreement with the

results of the temperature dependent studies. Solid line in Figure 3 represents the fit to the present data with sum of two exponential functions:

$$k_1 = 2.53\times10^{-11}\exp(-364/T) + 2.79\times10^{-13}\exp(784/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

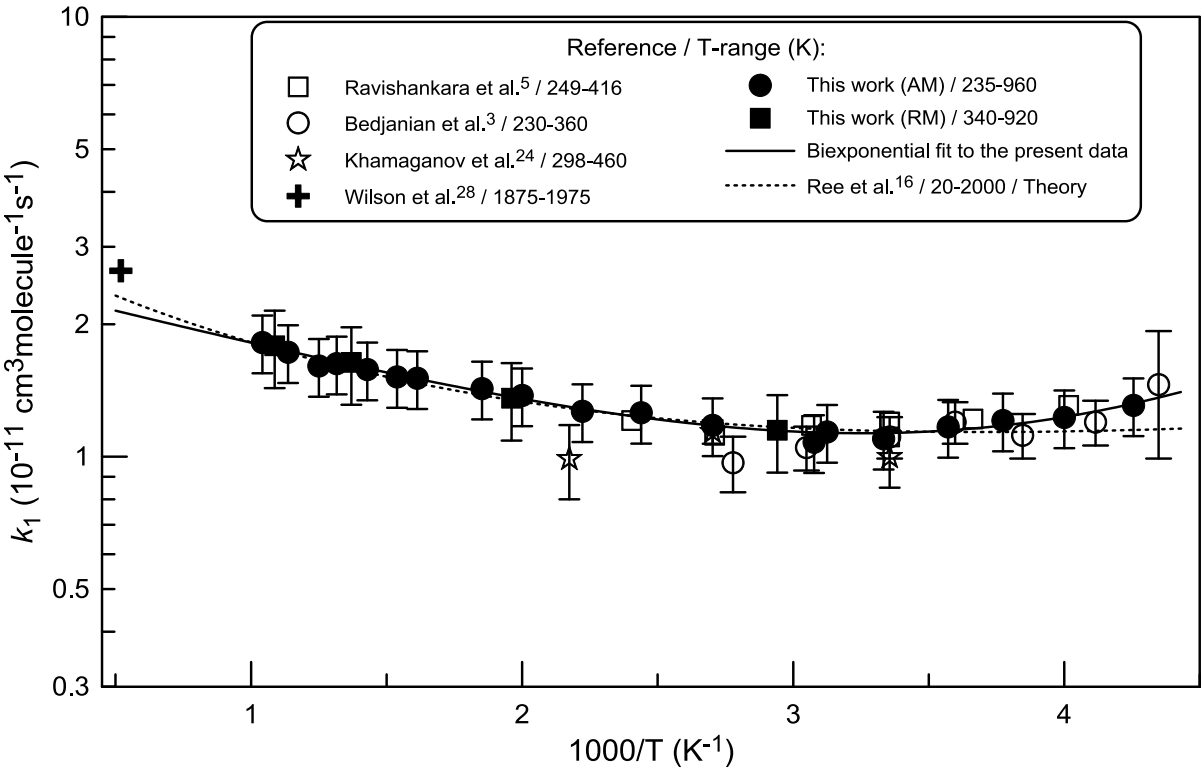

Figure 3. Summary of the data on the temperature dependence of the rate constant of reaction (1) in the temperature range of the present work.

Considering that, the present results are in excellent agreement with previous temperature dependent measurements of k_1, this expression can be recommended to use in the temperature range 230 – 960 K with conservative independent of temperature uncertainty of 15%. Interestingly, the extrapolation of the above expression for k_1 to T = 1925 K (see Figure 3) leads to $k_1 = (2.14\pm0.32)\times10^{-11}$ $\mathrm{cm^3molecule^{-1}s^{-1}}$, which is in a reasonable agreement with $k_1 = 2.66\times10^{-11}$ $\mathrm{cm^3molecule^{-1}s^{-1}}$, reported by Wilson et al. in their study on flame inhibition by HBr at T=(1875-1975) K.[28]

One can note surprisingly excellent agreement between the present experimental data and the results of theoretical calculations of k_1 by Ree et al.[16] in the whole temperature range of

the present work. Ree et al.[16] used a quasiclassical trajectory method (QCT) to calculate the temperature dependence of reaction (1) and shown that below room temperature, the reaction proceeds through formation of a collision complex with enhanced contribution of the H atom tunneling at low temperatures. At higher temperatures, according to the authors, the OH + HBr reaction occurs primarily through a direct H-atom abstraction mechanism. The expression recommended for the reaction rate constant at T = 20-2000 K reflected the proposed mechanism:

$$k_1 = 0.35\times10^{-11}(1+300/T)\exp(19/T) + 2.0\times10^{-11}(T/300)^{0.1}\exp(-626/T) + 0.15\times10^{-11}$$

(in $cm^3molecule^{-1}s^{-1}$ units), with the first and second terms representing primarily the complex and direct reaction paths at low and high temperatures, respectively.

All the available temperature dependent measurements of k_1 are shown in Figure 4 in line with some other theoretical calculations and evaluations of the rate constant covering high temperatures. In the work of Burgess et al.,[11] reporting a detailed chemical kinetic mechanism of the flame inhibition by the fire-suppressant 2-bromo-3,3,3-trifluoropropene, the following expression for the rate constant of reaction (1), $k_1 = 3.4\times10^{-13}\ T^{0.58}\exp(168/T)\ cm^3molecule^{-1}s^{-1}$, was proposed for use at flame temperatures. This expression reproduces quite well the temperature dependence of k_1 measured in the current study between 600 and 1000 K, with the absolute values of k_1 by ~20% higher compared with the experimental data. Similarly, the QCT calculations by Góger et al.[15] predict a small positive temperature dependence of k_1 at high temperatures, but in absolute value, they are by a factor of ≈ 1.8 lower at T> 600 K than the current experimental results.

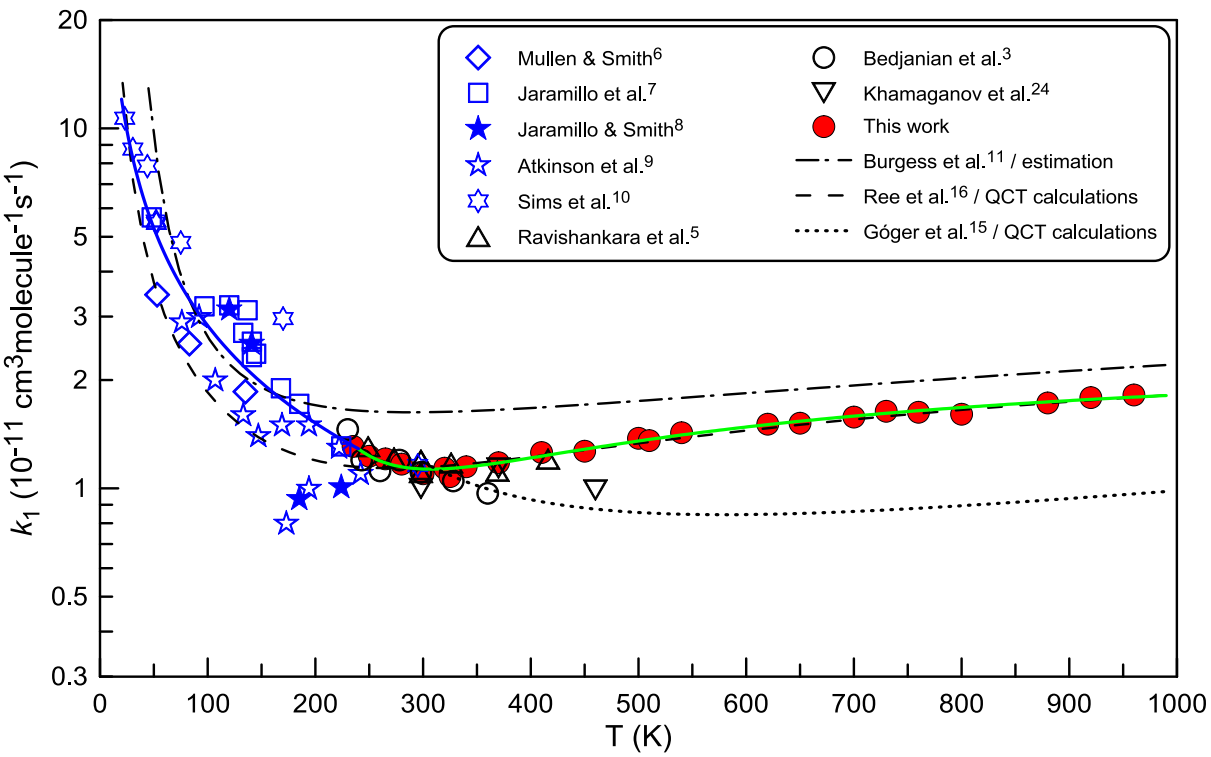

Figure 4. Summary of the temperature dependent measurements of the rate constant of reaction (1). The error bars are omitted for clarity.

Experimental data for k_1 obtained at ultralow temperatures using supersonic Laval nozzle flow reactors with monitoring of OH by laser induced fluorescence method[6-10] were analyzed by Mullen and Smith[6] who recommended $k_1 = (1.06\pm0.02)\times10^{-11}\ (T/298)^{(-0.9\pm0.11)}$ $cm^3molecule^{-1}s^{-1}$ in the temperature range 23-360 K. This expression obtained from the fit to the experimental data at low temperatures and that from the present work describing behavior of k_1 at high temperatures give identical (within 1%) results for k_1 at temperatures 240-270 K. On this basis, we recommend the following expressions for the rate constant of reaction (1):

$k_1 = 1.06\times10^{-11}\ (T/298)^{-0.9}$ $cm^3molecule^{-1}s^{-1}$ (23 -240 K),

$k_1 = 2.53\times10^{-11}\exp(-364/T) + 2.79\times10^{-13}\exp(784/T)$ $cm^3molecule^{-1}s^{-1}$ (T = 240-960 K),

which fairly well describe the temperature behavior of the rate constant over an extended temperature range 23-960 K (blue and green lines in Figure 4, respectively).

CONCLUSIONS

The rate constant of the reaction of OH radicals with HBr has been measured using a discharge flow reactor combined with an electron impact ionization mass spectrometer at T = 235 – 960 K: $k_1 = 2.53\times10^{-11}\exp(-364/T) + 2.79\times10^{-13}\exp(784/T)$ $cm^3molecule^{-1}s^{-1}$. This expression combined with that from previous low temperature measurements, $k_1 = 1.06\times10^{-11}(T/298)^{-0.9}$ $cm^3molecule^{-1}s^{-1}$ at T = 23-240 K, allows to describe the temperature behavior of the rate constant over a wide temperature range 23-960 K. The values of k_1 measured for the first time at high temperatures provide an experimental dataset for use in combustion and volcanic plume modelling and an experimental basis for validation and refining theoretical calculations.

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Supporting Information. Diagrams of the flow reactor (Figures S1a and S1b); examples of kinetics of OH consumption at different excess concentrations of HBr (Figure S2).

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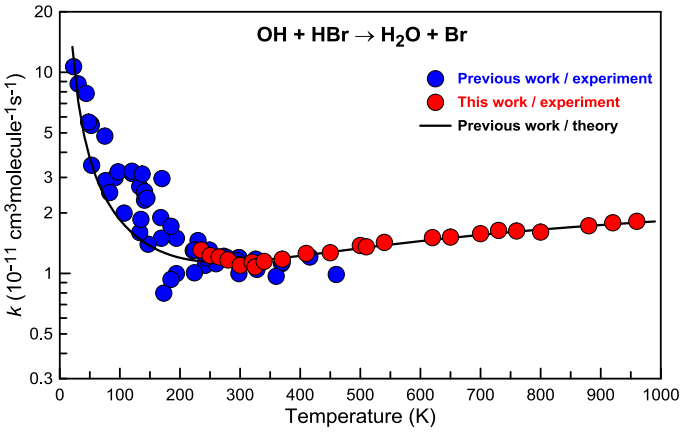
TOC Graphic


OH + HBr → H2O + Br
Previous work / experiment
This work / experiment
Previous work / theory
k (10-11 cm3molecule-1s-1)
20
10
5
3
2
1
0.5
0.3
0
100
200
300
400
500
600
700
800
900
1000
Temperature (K)