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Temperature Dependent Rate Constant for the Reaction of Hydroxyl Radical with 3-Hydroxy-3-Methyl-2-Butanone

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ABSTRACT

Reactions of hydroxyketones with OH radicals are of importance in atmospheric chemistry and represent a theoretical interest as proceeding through two reaction pathways, formation of hydrogen-bonded pre-reactive complex and direct H-atom abstraction. In this work, the kinetics of the reaction of OH radicals with 3-Hydroxy-3-Methyl-2-Butanone (3H3M2B) has been investigated at 2 Torr total pressure of helium over a wide temperature range, T = 278 – 830 K, using a discharge flow reactor combined with an electron impact ionization quadrupole mass spectrometer. The rate constant of the reaction OH + 3H3M2B $\rightarrow$ products (1) was determined using both relative rate method and absolute measurements under pseudo-first order conditions, monitoring the kinetics of OH consumption in excess of 3H3M2B, $k_1 = 5.44\times10^{-41}T^{9.7}\exp(2820/T)$ and $1.23\times10^{-11}\exp(-970/T)$ $cm^3molecule^{-1}s^{-1}$ at T = 278-400K and 400-830K, respectively (with total uncertainty of 20 % at all temperatures). The rate constant of the reaction OH + $Br_2 \rightarrow$ HOBr + Br (2) was measured as a part of this study using both absolute and relative rate methods: $k_2 = 2.16\times10^{-11}\exp(207/T)$ $cm^3molecule^{-1}s^{-1}$ at T = 220 -950K (with conservative 10% uncertainty). The kinetic data from the present study are discussed in comparison with previous measurements and theoretical calculations.

1. INTRODUCTION

3-Hydroxy-3-methyl-2-butanone ($(CH_3)_2C(OH)C(O)CH_3$) is a representative of hydroxyketones, chemical species belonging to a large family of Oxygenated Volatile Organic Compounds (OVOC) playing an important role in the tropospheric chemistry.[1] OVOCs are directly injected into the atmosphere as a result of anthropogenic and natural emissions, and can also be formed in the atmosphere upon degradation of primary emitted organic compounds. For example, hydroxyketones can be formed in the OH-initiated oxidation of alkanes,[2] alkane diols,[3] alkenes[4] and alcohols.[5] In particular, 3-Hydroxy-3-methyl-2-butanone was shown to be a product of OH-initiated oxidation of 2-methyl-2-butene in the presence of NO.[4] The atmospheric degradation of hydroxyketones is initiated by their reactions with atmospheric oxidants (OH, NO_3,O_3, Cl), mainly with OH radical, and their photolysis.[1] The understanding of the degradation mechanism of hydroxyketones in the atmosphere requires information on their major photo-oxidation pathways, including kinetics and primary products of their reactions with the atmospheric oxidants. Reactions of OH radicals with hydroxyketones are also of great theoretical interest as proceeding through a complex kinetic mechanism leading to a non-Arrhenius temperature dependence of the reaction rate constant. The existing data base on the reactions of hydroxyketones with OH is limited to a number of relative rate measurements at room temperature.[1] Even for the reaction of OH with the smallest hydroxyketone, hydroxyacetone, the dependence of the rate constant on temperature and its potential pressure dependence is a matter of discussion.[6] For the title reaction three experimental studies are available.[7-9] In two previous temperature-dependent studies of the reaction, realized in a rather narrow temperature range (277-356K), a slight positive[8] and slight negative[7] dependence of the reaction rate constant on temperature (with absolute values differing by up to a factor of 2) were reported. In addition, the reaction rate constant was theoretically calculated over the temperature range from 278 to 1000 K, showing slow decrease with temperature.[7] In this regard, the objective of the present work was to measure the rate constant of the reaction

$$OH + CH_3C(O)C(CH_3)_2OH \rightarrow \text{ products} \qquad (1)$$

in a wide temperature range and to compare it with previous experimental data and theoretical predictions.

In addition, the reaction of OH radicals with Br_2 was studied as a part of this study. This reaction is very often used in our laboratory for indirect detection of OH by mass spectrometry via conversion of the radicals to HOBr[10-12] and as a reference reaction in the relative measurements of OH reactivity:[13-14]

$$OH + Br_2 \rightarrow HOBr + Br \quad (2)$$

The rate constant of the reaction seems to be well established at low temperatures (T = 230-360K),[15-16] however, only one temperature dependence study is available at higher temperatures.[17] In the present work, we report the measurements of the rate constant in an extended temperature range, T = 220 – 950K.

2. EXPERIMENTAL

Experiments were carried out in a discharge flow reactor at total pressure of Helium of 2 Torr using a modulated molecular beam electron impact ionization quadrupole mass spectrometer (operated at 30 eV energy) as the detection method.[10-14] Two flow reactors were used. The first one, used at low temperatures (220 – 323 K), consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (ethanol) (Figure S1, Supporting Information (SI)).The walls of the reactor as well as of the movable injector of OH radicals were coated with halocarbon wax in order to minimize the heterogeneous loss of OH. The second flow reactor used at high temperatures (T = 299 – 950 K), consisted of an electrically heated uncoated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled attachments (Figure S2, SI).[18] Temperature in the reactor was measured with a K-type thermocouple positioned in the middle of the reactor in contact with its outer surface. Temperature variation along the flow tube (Figure S1, SI) measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1%.[18]

Hydroxyl radicals were produced in the movable injector through a rapid reaction of H atoms with excess NO_2 ($[NO_2] \sim 10^{13}$ molecule cm^{-3}), hydrogen atoms being generated in a microwave discharge of H_2/He mixtures (Figures S1 and S2, SI):

$$H + NO_2 \rightarrow OH + NO \quad (3)$$

$k_3 = (1.47 \pm 0.26) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (T = 195 – 2000).[19]

OH radicals were detected at m/z = 96/98 ($HOBr^+$) after being scavenged with an excess of Br_2 (added in the end of the reactor 5 cm upstream of the sampling cone, as shown in Figure S2, SI) through reaction 2:

$$OH + Br_2 \rightarrow HOBr + Br \quad (2)$$

$k_2 = 2.16\times10^{-11} \exp(207/T)$ $cm^3 molecule^{-1} s^{-1}$ (T = 220 – 950, this work).

This reaction was also used for the determination of the absolute concentrations of OH through their chemical conversion to HOBr in excess of Br_2: [OH] = [HOBr] = $\Delta[Br_2]$, i.e. concentration of OH (HOBr) was determined from the consumed fraction of $[Br_2]$. The possible influence of secondary chemistry on this method of the detection of OH radicals and their absolute calibration procedure was discussed in details in previous papers from this group.[12,15] In experiments on absolute measurements of the rate constant of reaction (2), OH radicals were detected also at m/z = 144 (HOI^+) upon their conversion to HOI in a rapid reaction with excess I_2 ($[I_2]$ = (1.0-1.5)×10^{13} molecule cm^{-3}, added in the end of the reactor by flowing Helium through a column containing iodine crystals, Figure S1, SI):

$$OH + I_2 \rightarrow HOI + I \quad (4)$$

$k_4 = (2.1 \pm 06)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} (T = 240 – 348).[16]

The 3-hydroxy-3-methyl-2-butanone (3H3M2B) was delivered to the reactor by flowing the bath gas (He) over liquid 3H3M2B and was detected by mass spectrometry at m/z = 59 ($C(CH_3)_2OH^+$) and its parent peak at m/z = 102 ($CH_3C(O)C(CH_3)_2OH^+$). The H_2O impurity in the gaseous samples of 3H3M2B, directly detected at m/z =18 (H_2O^+), was ≤ 1%. The absolute calibration of the mass spectrometer for 3H3M2B was realized under experimental conditions of kinetic measurements (pressure, temperature, total flow of bath gas, He) through injection of known amounts (0.2−1.0 μL) of 3H3M2B into the flow of helium and recording its parent peak intensity at m/z = 102. The integrated area of the mass spectrometric signal corresponding to known total number of 3H3M2B molecules injected into the reactor allowed the determination of the calibration factor. Absolute concentrations of stable species (NO_2, C_3H_8 and Br_2) were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks.

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); 3-hydroxy-3-methyl-2-butanone (> 95%, TCI Europe); Propane (>99.95%, Alphagaz).

3. RESULTS AND DISCUSSION

3.1. Rate constant of reaction (1): absolute measurements. The rate constant of the title reaction was determined under pseudo-first order conditions monitoring OH decays in excess of 3H3M2B, $[OH] = [OH]_0 \times \exp(-k_1' \times t)$, where [OH] and $[OH]_0$ are the time-dependent and initial concentrations of OH radicals, respectively, and $k_1' = k_1 \times [3H3M2B] + k_w$ is the pseudo-first-order rate constant with k_w representing the loss of OH radicals in the absence of 3H3M2B in the reactor. Initial concentration of OH radicals in these experiments was in the range $(1.5 - 3.5) \times 10^{11}$ molecule cm^{-3}; the concentrations of 3-hydroxy-3-methyl-2-butanone are shown in Table 1.

Table 1. Summary of the absolute measurements of the rate constants of the reaction OH + 3-hydroxy-3-methyl-2-butanone.

T (K)	Number of kinetic runs	[3H3M2B] (10^{13} molecule cm^{-3})	k_1[a] (10^{-13} $cm^3 molecule^{-1} s^{-1}$)
278	12	0.68-13.7	7.33
298	11	0.38-14.8	7.25
323	10	0.66-14.8	7.52
350	10	0.50-14.0	8.28
365	9	0.95-17.6	9.44
390	9	0.62-11.9	10.4
400	9	0.65-15.1	11.1
460	9	0.67-12.9	14.6
550	9	0.60-10.2	20.1
630	16	0.49-9.88	24.4
745	11	0.24-9.87	32.3
830	12	0.42-8.72	39.9

[a] Statistical uncertainty on k_2 is ≤ 5%, total estimated uncertainty is approximately 15%.

The flow velocity in the reactor was in the range (856-1695) cm s^{-1}. The pseudo-first-order rate constants were determined from the exponential fit to OH consumption kinetics: an example is shown in Figure 1. The consumption of the excess reactant, 3H3M2B, in reaction (1) was observed to be insignificant due to its sufficiently high excess over OH radicals. The

possible thermal decomposition of 3H3M2B at high temperatures of the study was also probed. Firstly, we have not observed any noticeable consumption of 3H3M2B on the time scale of our experiments. We have analyzed also the signals at m/z = 94/96, 96/98, 122/124, 138/140 and 166/168, corresponding to CH_3Br, HOBr, $CH_2C(O)Br$, $BrC(CH_3)_2OH$ and $BrC(O)C(CH_3)_2OH$, respectively, which could be formed in reactions of possible products of 3H3M2B decomposition with Br_2. The mass spectrometric signals corresponding to these species were found to be by at least a factor of 10 lower than those of OH radicals (detected as HOBr, see above) at highest concentrations of 3H3M2B and highest temperatures of the study. Given these observations, the thermal decomposition of 3H3M2B under experimental conditions of the study could be considered as insignificant and not affecting the rate constant measurements.

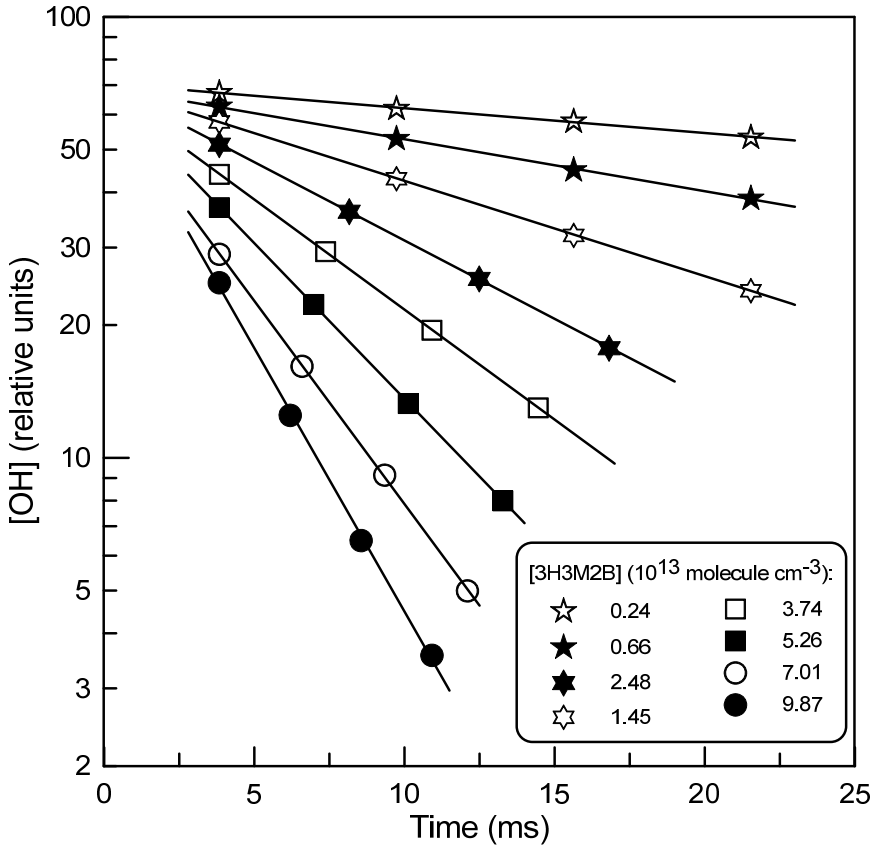

Figure 1. Examples of the exponential decays of OH in reaction with 3H3M2B at T = 745 K.

Examples of the dependencies of the pseudo-first order rate constant, k_1', on concentration of 3-hydroxy-3-methyl-2-butanone at different temperatures are shown in

Figure 2. All the measured values of k_1' were corrected for axial and radial diffusion of OH radicals[20] with diffusion coefficient of OH in He calculated as $D_0 = 660 \times (T/298)^{1.85}$ Torr cm^{-2} s^{-1}.[21] The applied corrections were generally within a few percent, although reaching up to 17% in a few kinetic runs.

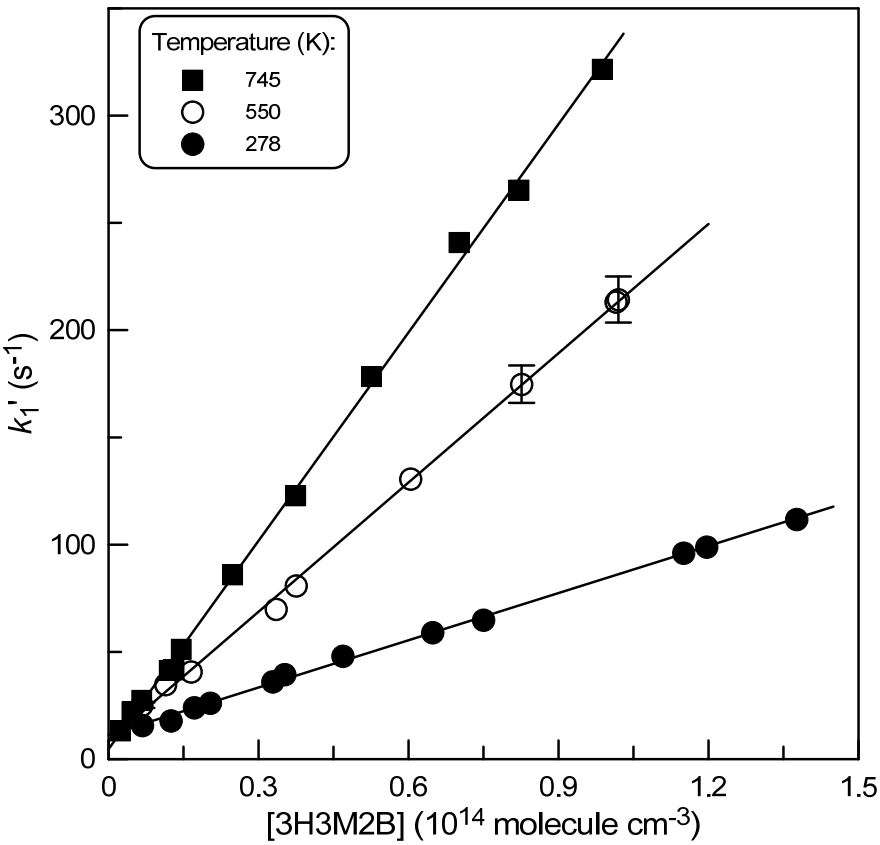

Figure 2. Pseudo-first-order rate constant (k_1') as a function of the concentration of 3H3M2B measured at different temperatures. Error bars represent typical uncertainties (≤ 5%) on the determination of k_1'.

The possible impact of secondary chemistry on the measurements of k_1 was tested in experiments with varied initial concentration of OH radicals. Figure S3 (SI) demonstrates the results of the measurements of k_1' with a fixed concentration 3H3M2B (8.0×10^{13} molecule cm^{-3}) and $[OH]_0$ varied in the range $(0.11 - 1.54) \times 10^{12}$ molecule cm^{-3}. The observed independence of k_1' of the initial concentration of OH radicals for $[OH]_0 < 10^{12}$ molecule cm^{-3} points to insignificant role of the secondary chemistry under the experimental condition of the measurements.

All the results of the absolute measurements of k_1 are shown in Table 1. The measurements of k_1 at temperatures between 278 and 350K have been carried out in a

Pyrex reactor coated with halocarbon wax and those at T ≥ 365K in an uncoated quartz reactor. The combined uncertainty on k_1 was estimated to be about 15% by adding in quadrature statistical error (≤ 5%) and those on the measurements of the flows (3%), pressure (2%), temperature (1%) and absolute concentration of 3-hydroxy-3-methyl-2-butanone (~10%).

3.2. Rate constant of reaction (1): relative measurements. Relative rate measurements were conducted with reaction of OH with Br_2 as a reference. Fast titration of the initial concentration of OH radicals, $[OH]_0$, by a mixture of Br_2 and 3H3M2B was performed, and the yield of HOBr was measured as a function of the $[3H3M2B]/[Br_2]$ ratio:

$$OH + 3H3M2B \rightarrow \text{products} \quad (1)$$

$$OH + Br_2 \rightarrow HOBr + Br \quad (2)$$

The concentration of HOBr formed is defined by the fraction of $[OH]_0$ reacting with Br_2 in reaction 2:

$$[\mathrm{HOBr}] = \frac{k_2[\mathrm{Br_2}]}{k_2[\mathrm{Br_2}]+k_1[\mathrm{3H3M2B}]+k_w} \times [\mathrm{OH}]_0$$

Rearrangement of this expression leads to:

$$\frac{[\mathrm{OH}]_0}{[\mathrm{HOBr}]} - 1 = \frac{k_1[\mathrm{3H3M2B}]}{k_2[\mathrm{Br_2}]} + \frac{k_w}{k_2[\mathrm{Br_2}]} \quad (\mathrm{I})$$

Experiments were carried out at constant concentration of Br_2 (to keep the contribution of the second term in equation (I) constant) and k_1/k_2 could be obtained by plotting ($[OH]_0/[HOBr]$ - 1) as a function of the $[3H3M2B]/[Br_2]$ ratio. This method did not need the measurements of the absolute concentrations HOBr and OH radicals because the initial concentration of OH, $[OH]_0$, could be expressed as HOBr signal in the absence of 3H3M2B in the reactor, when OH is titrated with an excess of Br_2. Thus, in the experiments, only the HOBr signal was detected: first, in 3H3M2B -free system, corresponding to $[OH]_0$, and then in the Br_2 and 3H3M2B -containing system, corresponding to the fraction of $[OH]_0$ reacted with Br_2. Reaction time was (0.015 – 0.030) s, initial concentration of OH atoms was in the range $(2\text{-}5)\times10^{11}$ molecule cm^{-3}, concentrations of Br_2 and 3H3M2B are shown in Table 2. At temperatures 285 and 310K, the measurements of k_1 were carried out in the reactor coated with halocarbon wax; the other measurements were performed in an uncoated quartz reactor. Examples of the observed experimental data are shown in Figure 3. According to equation (I), the slopes of the linear dependences in Figure 3 provide the values of k_1/k_2 at respective temperatures. Final values of k_1, shown in Table 2, were calculated with k_2 =

2.16×10^{-11} exp(207/T) $cm^3molecule^{-1}s^{-1}$ from this work which seems to be well established (within 10% uncertainty) at T = 220 -950K (see below). One can note, that two linear plots in Figure 3, corresponding to the data observed at T = 500K with different concentrations of Br_2, have similar slopes (i.e. provide similar k_1/k_2 ratios) and different intercepts in agreement with equation (I).

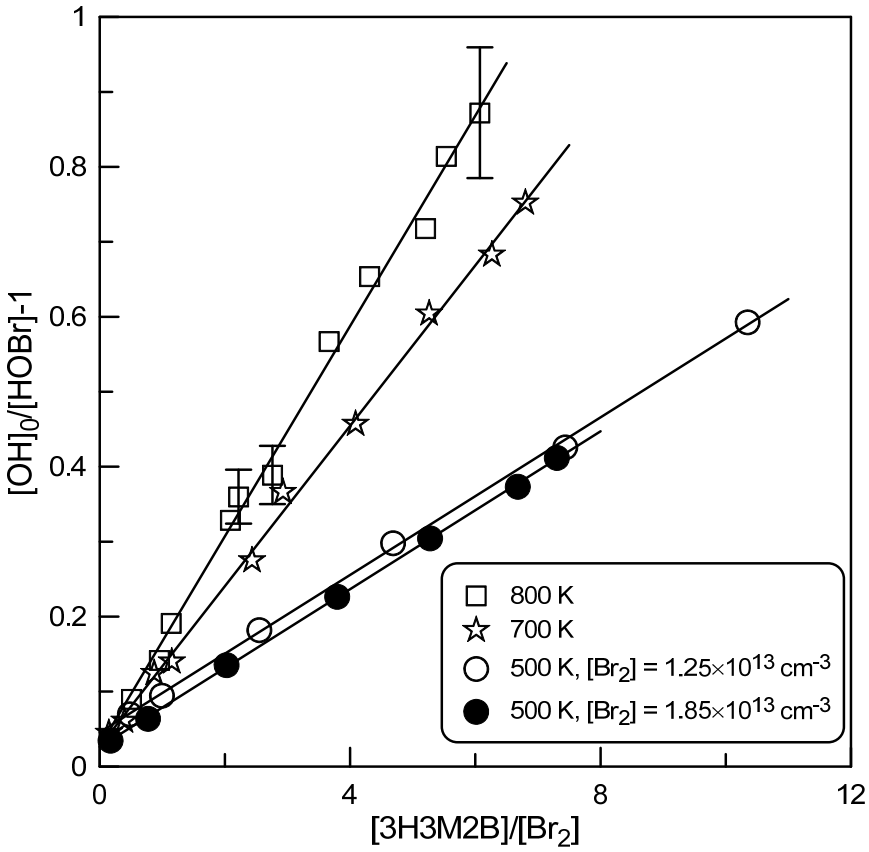

Figure 3. HOBr yield from OH radical titration with Br_2 + 3H3M2B mixtures at different temperatures. Partially shown error bars represent typical uncertainties of the measurements (≤ 10%).

Table 2. Experimental Conditions and Results of the Relative Measurements of the Rate Constant of the Reaction OH + 3-hydroxy-3-methyl-2-butanone.

T (K)	No./exp.[a]	[3H3M2B][b]	[Br_2][c]	k_1/k_2	k_1[d]
285	6	1.71-16.0	0.98	0.0166	7.41
310	13	0.32-11.1	0.94	0.0164	6.91
370	8	0.19-1.79	0.72	0.0257	9.71
420	8	0.22-1.71	1.02	0.0367	13.0
500	13	0.06-1.30	1.25-1.85	0.0526	17.2

700	10	0.02-0.98	1.48	0.107	31.1
800	11	0.09-1.03	1.75	0.140	39.2

[a] Number of data points. [b] Units of 10^{14} molecule cm^{-3}. [c] Units of 10^{13} molecule cm^{-3}. [d] Units of 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, estimated uncertainty on k_1 is approximately 20%.

3.3. Rate constant of reaction (2): absolute measurements. In the absolute study, the rate constant of the OH+Br_2 reaction was determined under pseudo-first order conditions from kinetics of OH consumption ($[OH]_0$ = (1.5 - 3)×10^{11} molecule cm^{-3}; detected as HOI, see Experimental section) in excess of Br_2 (see Table 3 for concentrations of Br_2). The flow velocity in the reactor was in the range (2150-3360) cm s^{-1}. Examples of OH decays at different concentrations of Br_2 are shown in Figure S4 (SI). The consumption of the excess reactant, Br_2, was observed to be insignificant (generally within a few percent), although reaching up to 15 % in a few kinetic runs at lowest concentrations of Br_2: in all cases the average concentration of excess reactant along the reaction zone was used in the calculation of the reaction rate constant. Figure 4 shows typical dependences of the pseudo-first-order rate constant, $k_2' = k_2 \times [Br_2] + k_w$, on concentration of Br_2. Diffusion corrections applied to k_2' were, as a rule, less than 10%.

Table 3. Summary of the absolute measurements of the rate constant of the reaction OH + Br_2.

T (K)	Number of kinetic runs	$[Br_2]$ (10^{13} molecule cm^{-3})	k_2[a] (10^{-11} $cm^3 molecule^{-1} s^{-1}$)
263	12	0.08-1.07	4.78
325	9	0.08-1.58	4.14
455	10	0.11-1.85	3.35
575	9	0.11-2.18	3.15
865	8	0.17-2.19	2.81

[a] Statistical uncertainty on k_2 is ≤ 5%, total estimated uncertainty is approximately 12%.

The intercepts in the examples shown in Figure 4 (as well as in other experiments), k_w, were in the range (20 ± 15) s^{-1}, in good agreement with the rate of OH decay measured in the absence of Br_2 in the reactor. All the results of the absolute measurements of k_2 are shown in Table 3. The combined uncertainty on k_2 was estimated to be ≈12% by adding in quadrature statistical error (≤ 5%) and those on the measurements of the flows (3%), pressure (2%), temperature (1%) and absolute concentration of Br_2 (≤ 10%).

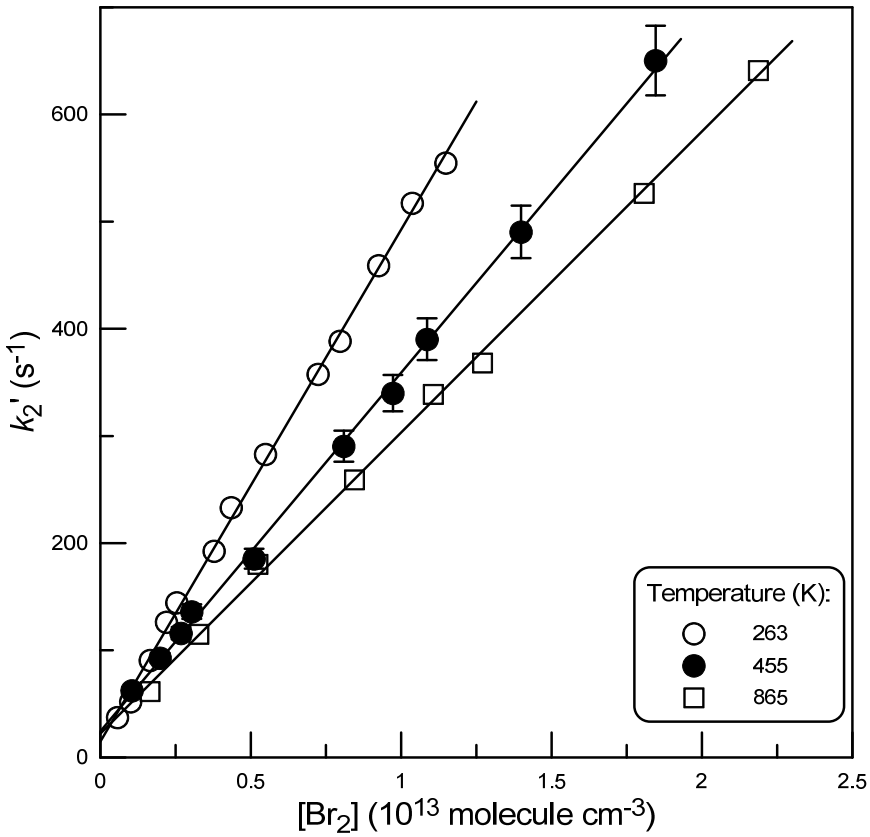

Figure 4. Pseudo-first-order rate constant (k_2') as a function of the concentration of Br_2 measured at different temperatures. Error bars represent typical uncertainties (≤ 5%) on the determination of k_2'.

3.4. Rate constant of reaction (2): relative measurements. In this series of experiments, we have carried out relative rate measurements with reaction of OH with propane as reference:

$$OH + Br_2 \rightarrow HOBr + Br \quad (2)$$

$$OH + C_3H_8 \rightarrow C_3H_7 + H_2O \quad (5)$$

Similarly to the relative measurements of k_1, upon titration of the initial concentration of OH radicals, $[OH]_0$, by a mixture of Br_2 and C_3H_8, the yield of HOBr was measured as a function of the $[C_3H_8]/[Br_2]$ ratio:

$$\frac{[OH]_0}{[HOBr]} - 1 = \frac{k_5[C_3H_8]}{k_2[Br_2]} + \frac{k_w}{k_2[Br_2]} \quad (II)$$

Reaction time was (0.02 – 0.04) s, initial concentration of OH radicals was in the range (2.5-6.5)×10^{11} molecule cm^{-3}, concentrations of Br_2 and C_3H_8 are shown in Table 4. Examples of the observed experimental data are shown in Figures 5 and S5 (SI). Final values of k_2, shown in Table 4, were calculated using the values of k_5/k_2 determined from the slopes of the linear

dependences in Figures 5 and S5 and $k_5 = 2.64\times10^{-17}T^{1.93}\exp(-114/T)$ $cm^3 molecule^{-1} s^{-1}$, which is well established over a wide temperature range T = 190 -1300K.[18]

Table 4. Experimental Conditions and Results of the Relative Measurements of the Rate Constant of the Reaction OH + Br_2.

T (K)	No./exp.[a]	$[C_3H_8]$ [b]	$[Br_2]$ [c]	k_2/k_5	k_2 [d]
220	11	1.36-40.7	0.86	107.1	5.59
235	11	0.46-20.0	0.02	84.0	5.14
255	11	0.52-18.5	0.75	64.5	4.80
275	12	0.28-15.7	0.90	51.3	4.57
299	11	0.42-10.7	0.87	40.8	4.41
345	11	0.44-5.80	0.78	26.0	3.90
410	11	0.20-6.48	1.35	16.2	3.57
505	12	0.20-5.45	1.50	9.35	3.25
660	11	0.18-3.29	2.13	4.76	2.92
790	12	0.08-1.18	2.90	3.12	2.79
950	11	0.04-0.97	1.25	2.03	2.65

[a] Number of data points. [b] Units of 10^{14} molecule cm^{-3}. [c] Units of 10^{13} molecule cm^{-3} [d] Units of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, estimated uncertainty on k_2 is approximately 15%.

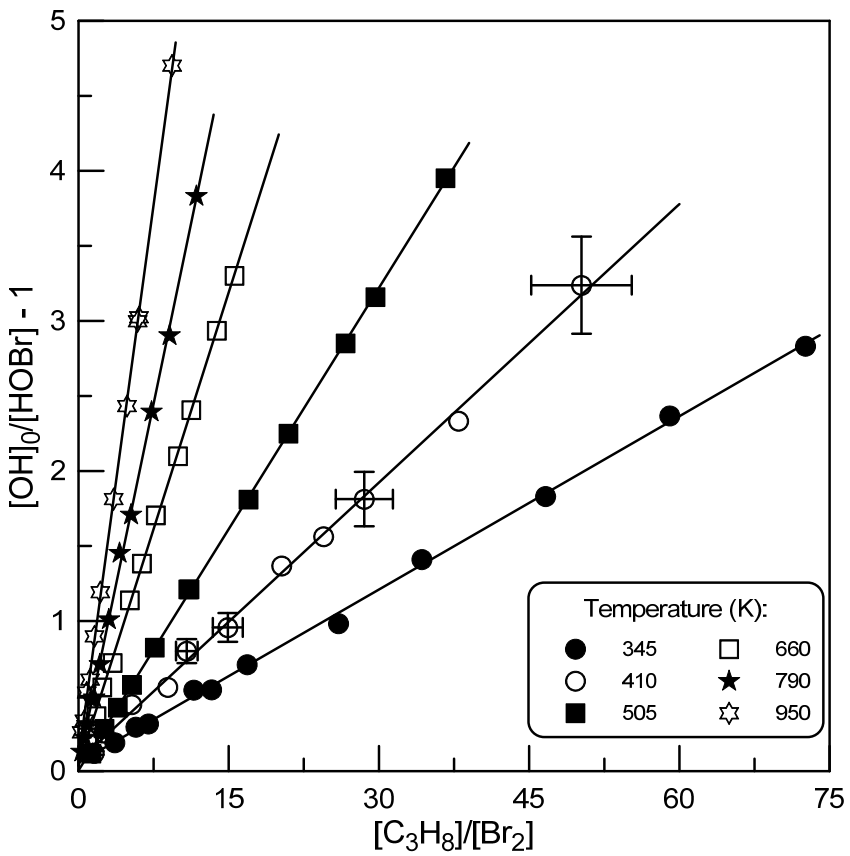

Figure 5. HOBr yield from OH radical titration with Br_2 + C_3H_8 mixtures at different temperatures. The horizontal and vertical error bars represent the estimated uncertainties (≤ 10%) on the respective values.

3.5. Comparison with previous studies. Figure 6 summarizes the results of the most recent temperature dependent measurements of the rate constant of reaction (2).

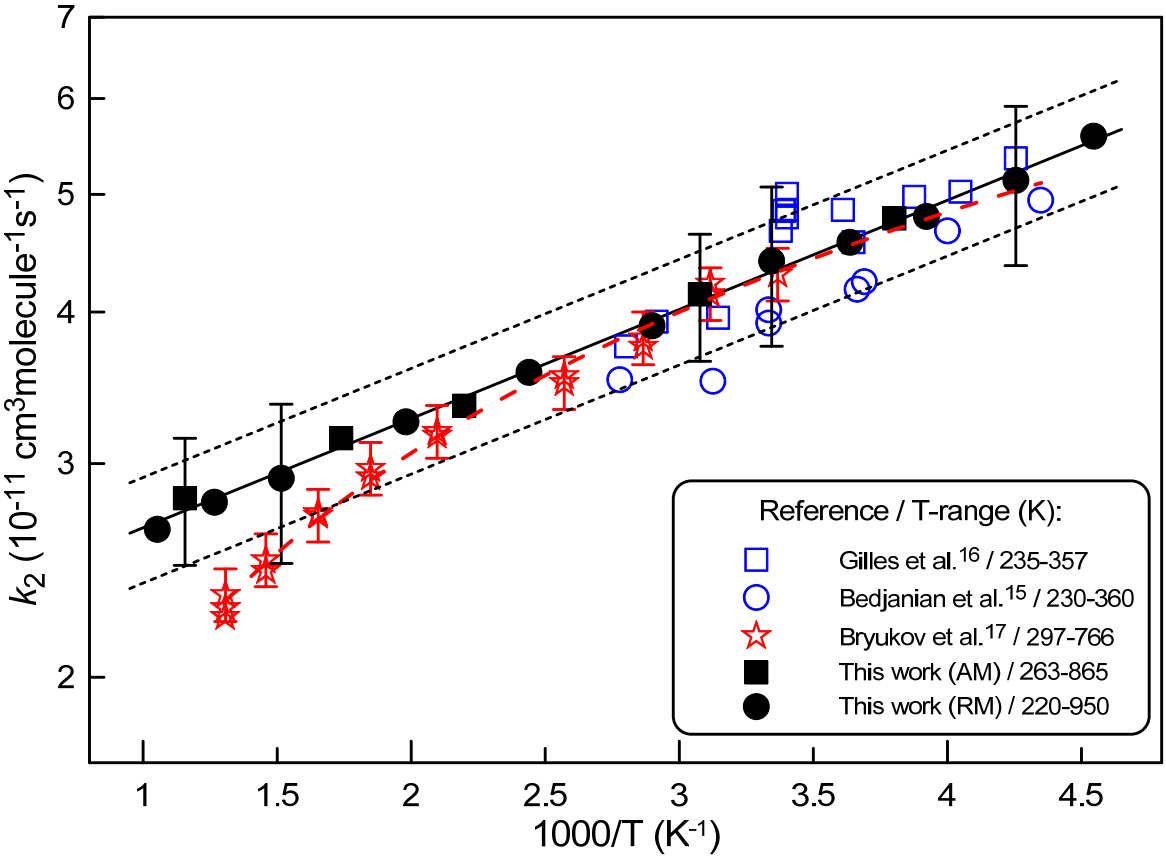

Figure 6. Reaction OH + Br_2: summary of the measurements of the temperature dependence of the reaction rate constant. AM: absolute measurement, RM: relative rate method. Partially shown error bars correspond to estimated 12 and 15 % uncertainty on the measurements of k_2 in the present work by absolute and relative rate method, respectively, and to maximum systematic uncertainty of 5% estimated in ref. 17. Uncertainties on k_2 reported in two other previous studies are omitted for clarity. Red dashed line: previous recommendation;[17] black solid line: Arrhenius fit to the present data; dotted lines: present fit ±10%.

Gilles et al.[16] have measured the reaction rate constant, k_2 = (1.98±0.51)×10^{-11} exp((238±70)/T) cm^{3}molecule^{-1}s^{-1} at T = 235-357K, under pseudo-first-order conditions in OH by using a pulsed laser photolysis/laser-induced fluorescence (PLP/LIF) technique. In the earlier study from our group,[15] the reaction rate constant, k_2 = (1.8±0.3)×10^{-11} exp((235±50)/T)cm^{3}molecule^{-1}s^{-1} at T = 230 -360K, was derived both from the kinetics of Br_2 consumption in excess of OH radicals and HOBr formation kinetics in excess of Br_2. The results from two studies are in excellent agreement and show a slight negative temperature

dependence of k_2. In the only high temperature study of reaction (2), Bryukov et al.[17] using PLP/LIF method extended the measurements of k_2 to 766K and recommended k_2 = $(1.85\pm0.32)\times10^{-9} \times T^{-0.67\pm0.03}$ $cm^3molecule^{-1}s^{-1}$ at T = 230 -766K. As one can see in Figure 6, the experimental data from the present work are in excellent agreement with previous measurements of k_2, except those of Bryukov et al.[17] at highest temperatures of their study, where a downward curvature in the Arrhenius plot was observed. The reason for this slight disagreement (the reported uncertainty ranges overlap) is unknown. It can be noted that the observed experimentally downward curvature in the Arrhenius plot was not supported by theoretical calculations realized by Bryukov et al.:[17] the computed temperature dependence of k_2 displayed a slight upward curvature at high temperatures. Least-squares fit to k_2 data from the present work (solid line in Figure 6) provides the following Arrhenius expression:

$k_2 = 2.16\times10^{-11} \exp(207/T)$ $cm^3molecule^{-1}s^{-1}$ at T = 220 -950K.

Fit of the data from the present work combined with the two previous low temperature measurements[15-16] results in an identical Arrhenius expression. The dotted lines in Figure 6 correspond to ± 10% deviation from this expression, showing that practically all temperature dependent data for k_2 fall into this range. Based on this, we would recommend the above expression for k_2 for use in the temperature range 220–950 K with conservative 10% uncertainty.

The temperature dependence of k_1 observed in the present work is shown in Figure 7 along with previous measurements.[7-9] Aschmann et al.[9] and Bouzidi et al.[8] have carried out relative rate measurements of the rate constant of reaction (1). The rate constant, k_1 = $(0.94\pm0.37)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ at 296 K, originally reported by Aschmann et al.,[9] when placed on an absolute basis by use of a new recommendation for the reference reaction OH + n-octane, results in k_1 = $(0.85\pm0.33)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$.[1] Priya et al.[7] have carried out absolute measurements of the rate constant of reaction (1) over the temperature range 277 - 353 K and total pressure between 5 and 80Torr, by using PLP/LIF technique. One can see in Figure 7 that the present data obtained at 2 Torr total pressure are in good agreement with previous relative measurements of Aschmann et al.[9] and Bouzidi et al.[8] realized at 740 and 500-600 Torr total pressure, respectively. This can be considered as an indication that the rate constant of reaction (1) does not depend (at least substantially) on pressure. The present data for k_1 are by a factor of 1.3-1.9 higher than the absolute measurements of Priya et al.[7] It is difficult to establish the exact cause of this discrepancy. One of the possible

options is the measurements of the absolute concentrations of 3H3M2B. In the present work, 3H3M2B was directly monitored with mass spectrometer and absolute calibration of the 3H3M2B signals was realized by injecting known amounts of liquid 3H3M2B inside the flow tube as described in Experimental section. In the study of Priya et al.[7] the concentrations of 3H3M2B in the reaction zone were calculated from mass flow rates of 3H3M2B/He mixtures stored in a 20 L bulb. This method could potentially lead to overestimation of the 3H3M2B concentrations. Indeed, we have observed a decrease in gaseous concentration of 3H3M2B over time (from day to day) during the storage of 3H3M2B/He mixtures in 10L Pyrex flask. This may be due to the adsorption of 3H3M2B on the surface of the flask, its decomposition, or other reasons; we did not attempt to carry out specific experimental work to clarify this issue.

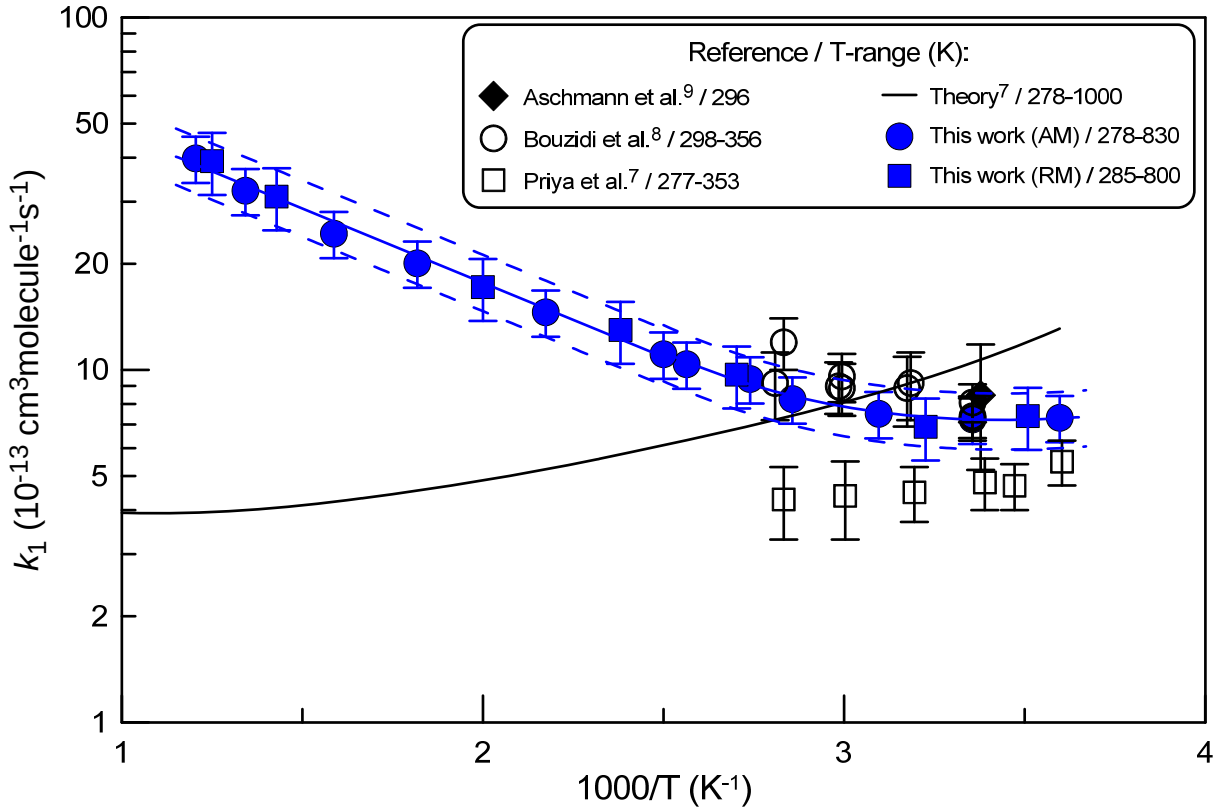

Figure 7. Reaction OH + 3-hydroxy-3-methyl-2-butanone: summary of the measurements of the reaction rate constant. AM: absolute measurement, RM: relative rate method. The error bars correspond to estimated 15 and 20 % uncertainty on the measurements of k_1 in the present work by absolute and relative rate method, respectively; uncertainties on previous measurements are given as reported in respective studies.

The present data are in contradiction with theoretical calculations of Priya et al.[7] (black solid line in Figure 7), in particular, with the statement of the authors that "the calculated theoretical rate constants are in good agreement with the experimental data over the

temperature range of 278 to 1000 K".[7] Our experimental data exhibit positive temperature dependence, while computed k_1 decreases with temperature. The computed and experimental values of k_1 at T ≈ 800 K, highest temperature of this study, differ by an order of magnitude.

As one can see in Figure 7, in the present work, the rate constant of reaction (1) was observed to be temperature independent at T = 278-323K and increasing at higher temperatures. This non-Arrhenius behavior could be expected. Similarly to reaction of OH with hydroxyacetone (smallest hyrdoxyketone)[6,22] and also with aldehydes and ketones,[1] reaction (1) can proceed via two mechanisms, through formation of hydrogen-bonded pre-reactive complex and direct H-atom abstraction with major contributions of these pathways at lower and higher temperatures, respectively. This mechanism, in combination with tunneling effect at low temperatures, results in non-Arrhenius, often U-shaped, behavior of the reaction rate constant observable experimentally if a sufficiently wide temperature range is considered.[1] In this regard, even upward curvature in the temperature dependence of k_1 can be expected at lower temperatures. Unfortunately, our measurements were limited to T = 278K because of the heterogeneous complications at lower temperatures, which were manifested in an anomalous increase of the OH consumption rate in the presence of even very low concentrations of 3H3M2B, probably due to reaction of OH with 3H3M2B on the surface of the flow reactor. At higher temperatures we have not observed any evidence of the heterogeneous reaction. In this regard, it can be noted that compatible values of k_1 were measured in different reactors at close temperatures (at T = 350 and 365K in halocarbon wax coated and uncoated quartz reactors, respectively). Finally, the present experimental data were fitted with Arrhenius expression at T = 400 – 830K and modified Arrhenius expression at T = 278 – 400K (blue solid lines in Figure 7), leading to:

$k_1 = 5.44\times10^{-41}T^{9.7}\exp(2820/T)$ cm^{3}molecule^{-1}s^{-1} (T = 278-400K),

$k_1 = 1.23\times10^{-11}\exp(-970/T)$ cm^{3}molecule^{-1}s^{-1} (T = 400-830K)

with conservative temperature independent 20% uncertainty (dashed lines in Figure 7). It is clear that the expression for k_1 at T = 278-400K has no physical meaning and should be considered only as a representation of the rate coefficients in this temperature range.

The tropospheric lifetime of 3-Hydroxy-3-Methyl-2-Butanone with respect to its gas phase reaction with OH, 16 days (calculated using the measured rate constants of 7.25×10^{-13} cm^{3}molecule^{-1}s^{-1} at T=298 K and a 24 h average concentration of OH radical of 10^6 molecules

cm^{-3}), is comparable with atmospheric lifetime of 3H3M2B of 4-5 days with respect to its photolysis[8] and supports the conclusions of the previous studies[7-9] on importance of the reaction (1) as a tropospheric loss process of 3H3M2B.

CONCLUSIONS

In this work, we investigated the kinetics of the reaction of OH radicals with 3-Hydroxy-3-Methyl-2-Butanone (3H3M2B) using a discharge flow reactor combined with an electron impact ionization mass spectrometer. The total rate constant of the reaction, $k_1 = 5.44\times10^{-41}$ $T^{9.7}\exp(2820/T)$ and 1.23×10^{-11} $\exp(-970/T)$ $cm^3molecule^{-1}s^{-1}$ at T = 278-400K and 400-830K, respectively, was determined using both absolute and relative rate method for temperatures in the range 278 -830 K. Temperature dependence of k_1, measured over a wide temperature range, is significantly different from that of available computational study and, apparently, is an interesting experimental basis for further theoretical developments. The temperature dependence of the rate constant of the OH + Br_2 reaction, measured as a part of this study, $k_2 = 2.16\times10^{-11}$ $\exp(207/T)$ $cm^3molecule^{-1}s^{-1}$, and found to be in good agreement with previous data, was extended to lower (T = 220K) and higher (T = 950K) temperatures.

ASSOCIATED CONTENT

Supporting Information. Diagrams of the low and high temperature flow reactors (Figures S1 and S2, respectively); dependence of k_1' on initial concentration of OH radicals (Figure S3); examples of the exponential decays of OH in reaction with Br_2 (Figure S4); HOBr yield from OH radical titration with Br_2 + C_3H_8 mixtures at different temperatures (Figure S5).

ACKNOWLEDGEMENT

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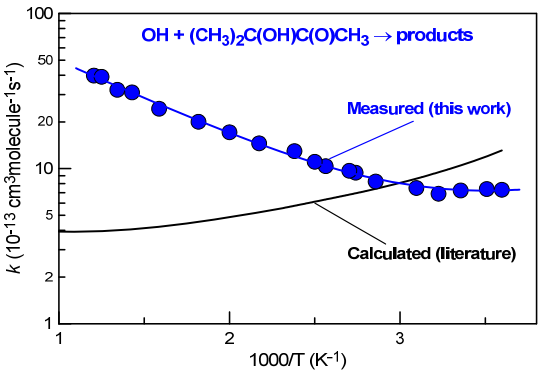
TOC Graphic


OH + (CH3)2C(OH)C(O)CH3 → products
Measured (this work)
Calculated (literature)
k (10-13 cm3molecule-1s-1)
1000/T (K-1)
100
50
20
10
5
2
1
1
2
3