Experimental Study of the Reactions of OH Radicals with Propane, n-Pentane and n-Heptane over a Wide Temperature Range.

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ABSTRACT: The kinetics of the reactions of propane, n-pentane and n-heptane with OH radicals has been studied using a low pressure flow tube reactor coupled with a quadrupole mass spectrometer. The rate constants of the title reactions were determined under pseudo-first order conditions, monitoring the kinetics of OH radical consumption in excess of the alkanes. A newly developed high temperature flow reactor was validated by the study of OH + propane reaction, where the reaction rate constant, $k_1 = 5.1 \times 10^{-17} T^{1.85} \exp(-160/T)$ $cm^3 molecule^{-1} s^{-1}$ (uncertainty of 20%), measured in a wide temperature range, 230 – 898 K, was found to be in excellent agreement with previous studies and current recommendations. The experimental data for the rate constants of the reactions of OH with n-pentane and n-heptane can be represented as three parameter expressions (in $cm^3 molecule^{-1} s^{-1}$, uncertainty of 20%): $k_2 = 5.8 \times 10^{-18} T^{2.2} \exp(260/T)$ at T = (248 – 900) K and $k_3 = 2.7 \times 10^{-16} T^{1.7} \exp(138/T)$ at T = (248 - 896) K, respectively. Combination of the present data with those from previous studies leads to the following expressions: $k_1 = 2.64 \times 10^{-17} T^{1.93} \exp(-114/T)$, $k_2 = 9.0 \times 10^{-17} T^{1.8} \exp(120/T)$ and $k_3 = 3.75 \times 10^{-16} T^{1.65} \exp(101/T)$ $cm^3 molecule^{-1} s^{-1}$, which can be recommended for k_1, k_2 and k_3 (with uncertainty of 20%) in the temperature ranges (190 – 1300), (240 - 1300) and (220 – 1300) K, respectively.

Keywords: Hydroxyl radical, propane, n-pentane, n-heptane, kinetics, rate coefficient.

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INTRODUCTION

Alkanes represent an important class of volatile organic compounds [1] emitted into the atmosphere from both anthropogenic and natural sources. They are released in large amounts in activities connected with the extraction, conditioning and combustion of fossil fuels, combustion and microbiological degradation of organic matter. Alkanes play an important role in tropospheric chemistry and, in particular, in photochemical ozone formation [2]. The atmospheric oxidation of alkanes, initiated mainly by their reaction with OH radicals, leads to the formation of oxygenated organic compounds such as acetone, formaldehyde and acetaldehyde. Hence, alkanes significantly influence the atmospheric HO_x ($OH+HO_2$) budget through many complex reaction cycles [2]. Primary step of the degradation of alkanes, reaction with OH radicals, is an important process not only in the atmosphere, but also in combustion of various fuels containing a large variety of alkanes [3]. Thus, there is a need for direct and precise measurements of the rate constants of the reactions of OH with alkanes in a wide temperature range, from ambient temperatures to those in combustion processes.

In the present work, we report the measurements of the rate constants of the reactions of OH with propane, n-pentane and n-heptane at temperatures between 230 and 900 K:

$$OH + C_3H_8 \rightarrow products \tag{1}$$

$$OH + n\text{-}C_5H_{12} \rightarrow products \tag{2}$$

$$OH + n\text{-}C_7H_{16} \rightarrow products \tag{3}$$

The well-known reaction of OH with propane [4-7] was chosen as a reference one in order to validate the newly developed high temperature flow reactor, used for the first time in this work. As for the reactions of OH with n-pentane and n-heptane, the existing kinetic data are limited to low (T < 400K) and high (T > 800K) temperatures [8]. One of the objectives of this study was to address the lack of the kinetic data at intermediate temperatures between 400 and 800 K in order to harmonize the high temperature shock tube studies with those at low temperatures.

EXPERIMENTAL

Experiments were carried out in a discharge flow reactor using a modulated molecular beam mass spectrometer as the detection method [9-13]. Two flow reactors were used in the present work. The first one, used at low temperatures (230 – 350K), consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (water or ethanol)

[9-13]. The walls of the reactor as well as of the movable injector of OH radicals were coated with halocarbon wax (HW) in order to minimize the heterogeneous loss of OH.
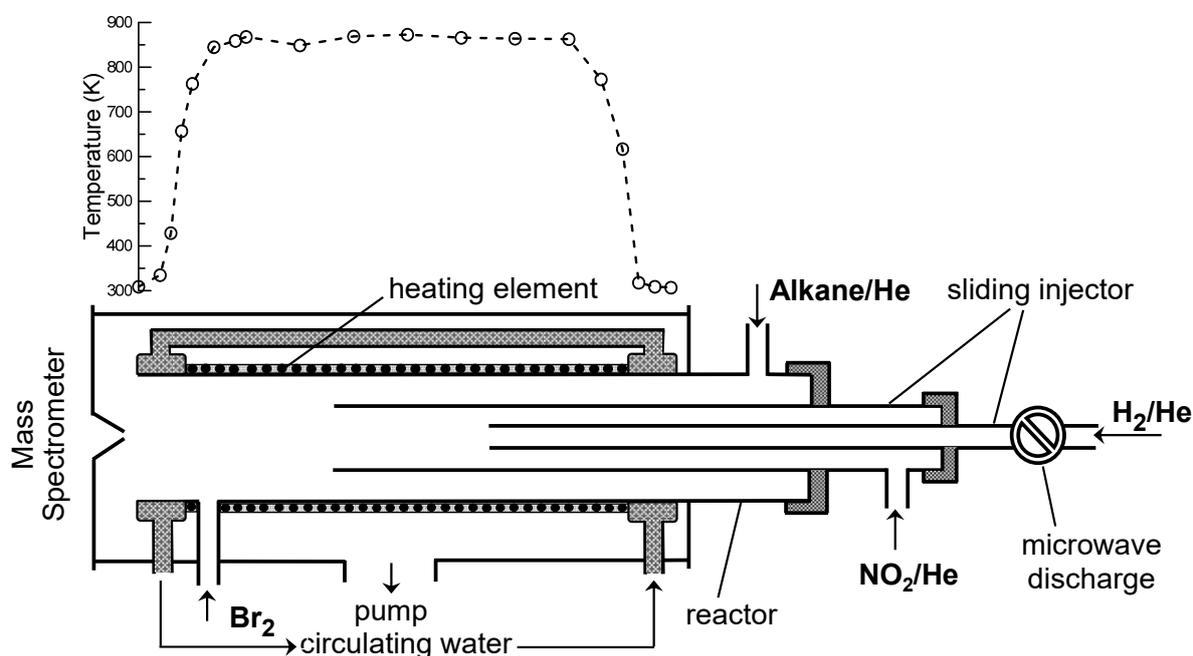

Figure 1 Diagram of the flow reactor.

The second flow reactor, which was developed in the present work for kinetic studies at high temperatures (T = 300 – 1000 K), consisted of an electrically heated Quartz tube (45 cm length and 2.4 cm i.d.) with water-cooled extremities (Fig. 1). 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 gradient along the flow tube (Fig. 1) measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1%. In order to reduce the heterogeneous loss of OH radicals at high temperatures the walls of this reactor were coated with boric acid (BA). The inner surface of the reactor was first treated with a 5% solution of boric acid in water and then dried.

OH radicals were generated via fast reaction of hydrogen atoms with NO_2, H atoms being produced in a microwave discharge of H_2/He mixture:

$$H + NO_2 \rightarrow OH + NO \tag{4}$$

$$k_4 = (1.47 \pm 0.26) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (T = 195 – 2000) [14]}$$

NO_2 was always used in excess over H atoms. OH radicals were detected as $HOBr^+$ (m/z = 96/98) after scavenging by an excess of Br_2 ([Br_2] = (5-10) $\times 10^{13}$ molecule cm^{-3}, added at the end of the reactor, 5 cm upstream of the sampling cone) via reaction:

OH + Br$_2$ → HOBr + Br (5)

$k_5 = 1.96 \times 10^{-9}$ T$^{-0.67}$ cm^3 molecule^{-1} s^{-1} (T = 230 – 766) [15]

This method for OH detection was preferred to the direct detection of these radicals at m/z = 17 (OH$^+$) due to significant contribution of water traces, present in the reactor, at this mass. Similarly, the chemical conversion of OH to HOBr was used for the measurements of the absolute concentrations of the radicals: [OH] = [HOBr] = Δ[Br$_2$], i.e. concentrations of OH were determined from the consumed fraction of [Br$_2$]. [Br$_2$] was determined from the measured flow rate of known Br$_2$/He mixtures. The possible influence of secondary chemistry on this method of HOBr detection and their absolute calibration procedure was discussed in details in previous papers from this group [9,10].

All species were detected at their parent peaks: m/z= 44 (propane, C$_3$H$_8$$^+$), 72 (pentane, C$_5H_{12}$$^+$), 100 (heptane, C$_7H_{16}$$^+$), 160 (Br$_2$$^+$), 96/98 (HOBr$^+$), 46 (NO$_2$$^+$). The absolute concentrations of alkanes in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of alkane/He mixtures stored in calibrated volume flasks.

The purities of the gases used were as follows: He >99.9995% (Alphagaz), was passed through liquid nitrogen trap; H$_2$ > 99.998% (Alphagaz); Br$_2$ >99.99% (Aldrich); NO$_2$ > 99% (Alphagaz), propane > 99.95% (Alphagaz); n-pentane > 99.5% (Fluka); n-heptane > 99% (Sigma-Aldrich).

RESULTS AND DISCUSSION

Reaction OH + Propane

The measurements of the rate constant of reaction (1) were carried out under pseudo-first order conditions in high excess of propane over OH radicals. The initial concentration of OH radicals was nearly 5×10^{11} molecule cm^{-3}, the concentrations of propane are shown in Table I.

Table I Reaction OH + Propane: Summary of the Measurements of the Rate Constant

T (K)	Reactor Coating[a]	Number of Kinetics	[Propane] (10^{14} molecule cm^{-3})	k_1 (10^{-12} cm^3 molecule^{-1} s^{-1})[b]
230	HW	7	0.52-5.18	0.59
248	HW	7	0.31-3.89	0.69
268	HW	9	0.26-4.06	0.89
300	HW	7	0.31-3.57	1.15

343	HW	7	0.33-2.27	1.49
419	BA	6	0.18-2.49	2.45
476	BA	7	0.13-1.93	3.31
562	BA	6	0.12-1.13	4.38
686	BA	5	0.08-0.93	7.11
781	BA	7	0.08-0.77	10.04
898	BA	7	0.06-0.63	11.97

[a] HW: halocarbon wax; BA: boric acid.
[b] typical uncertainty on k_1 is (15 – 20) %.

The flow velocity in the reactor was (1245-4420) cm s^{-1}. The concentrations of OH radical and propane were simultaneously measured as a function of reaction time. A consumption of propane was negligible as a result of its high excess over OH radicals. Examples of the exponential decay kinetics of OH in reaction with propane are shown in Fig. 2.
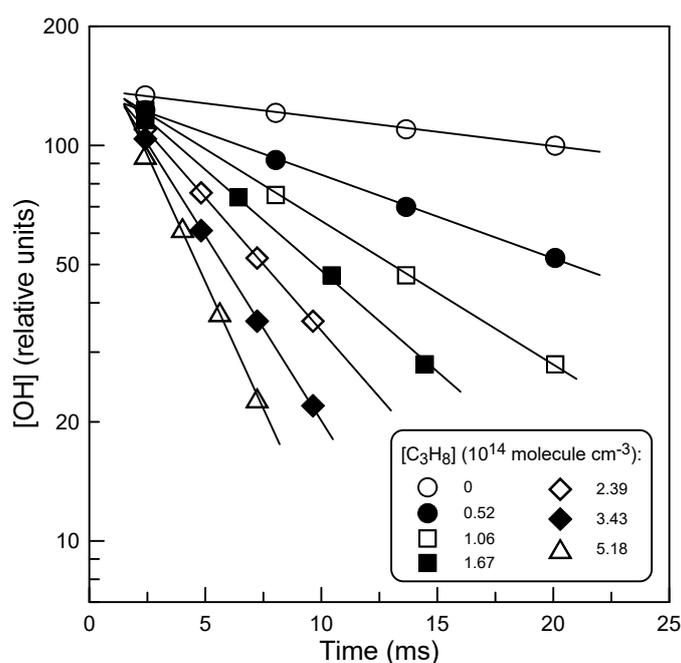

Figure 2 Reaction OH + C_3H_8: example of the exponential decays of OH in excess of propane at T = 230 K.

Figure 3 shows the pseudo-first order rate constant, $k_1' = k_1[C_3H_8] + k_w$, as a function of the concentration of propane. k_w represents the rate of OH decay in the absence of propane in the reactor and was measured in separate experiments. All the measured values of k_1' were corrected for axial and radial diffusion [16] of OH. The diffusion coefficient of OH in He was calculated using the following expression: $D_0 = 640 \times (T/298)^{1.85}$ Torr cm^2 s^{-1} [17-19]. Corrections were generally less than 10%, and only in a few kinetic runs they were higher

with a maximum of 18%. The slopes of the straight lines in Fig. 3 give the values of k_1 at respective temperatures. The intercepts were in the range (25 ± 10) s^{-1} without an appreciable dependence on temperature and in good agreement with the corresponding OH loss rate measured in the absence of propane in the reactor.
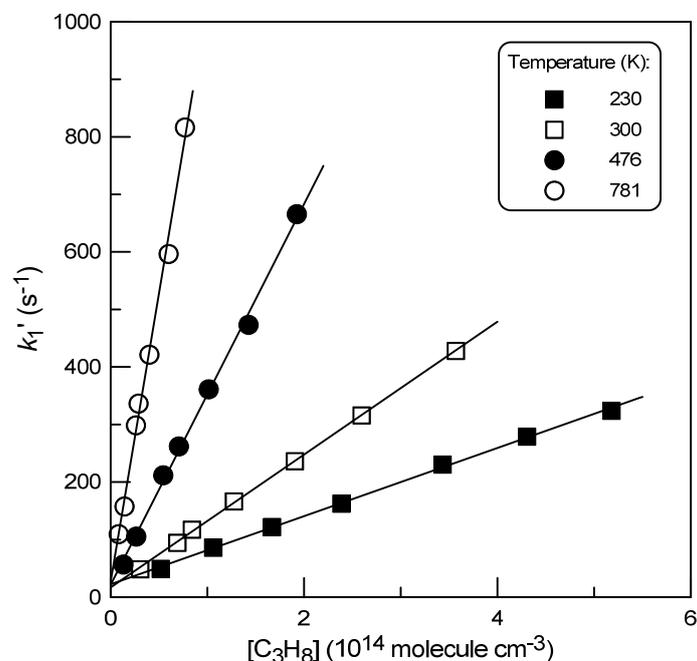

Figure 3 Reaction OH + C_3H_8: example of pseudo-first order plots obtained from OH decay kinetics at different temperatures.

All the results obtained for k_1 at different temperatures are shown in Table I and Fig. 4. The combined uncertainty on the measurements of the rate constants was estimated to be in the range of 15-20%, including statistical error (within a few percent) and those on the measurements of the flows (5%), pressure (3%), temperature (1%), and the absolute concentrations of alkane ($\leq 10\%$).

The possible influence of secondary chemistry on the measurements of k_1 was explored in separate experiments at T = 300 K, where the rate of reaction (1) was measured at fixed concentration of propane (3.3×10^{14} molecule cm^{-3}) and initial concentration of OH radicals varied in the range $(0.3 - 1.5) \times 10^{12}$ molecule cm^{-3}. The pseudo-first order rate constant, $k_1' \approx 400$ s^{-1}, was found to be independent (within a few %) of $[OH]_0$, indicating the negligible contribution of the secondary reactions to the OH loss.
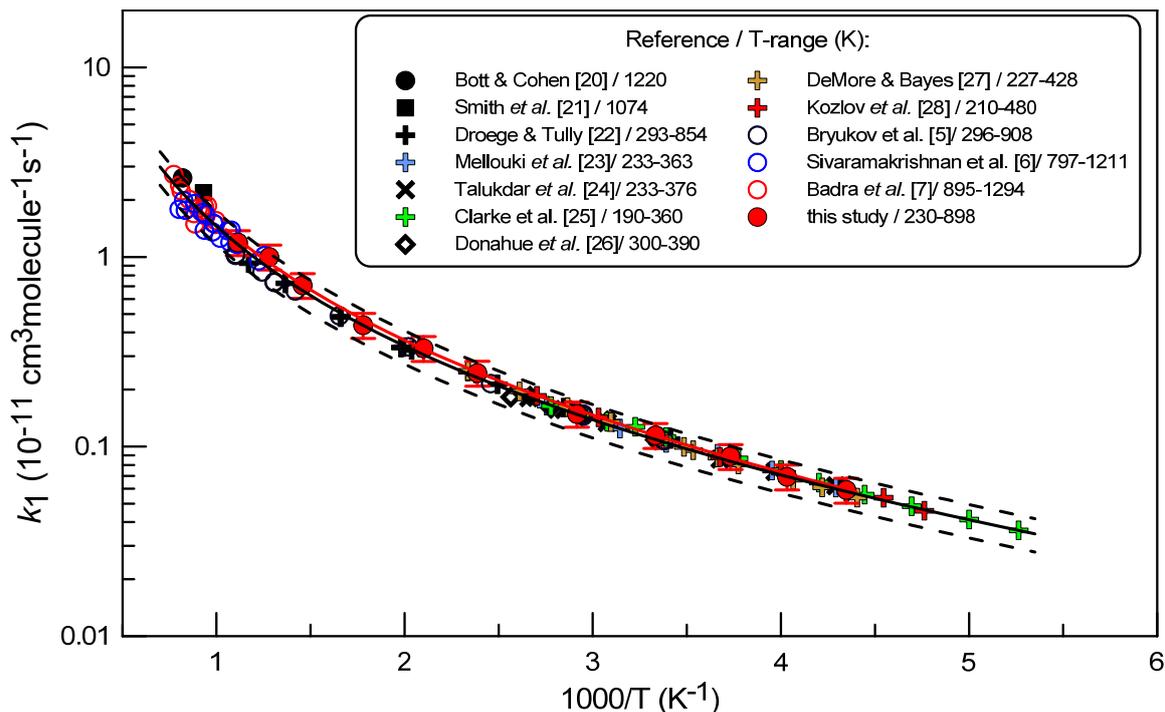
Figure 4 Reaction OH + C_3H_8: summary of the measurements of the temperature dependence of the rate constant. Error bars correspond to 15% uncertainty on k_1. Red solid line: three parameter fit to the present data; black solid line: fit to all data; dashed line: fit to all data $\pm$ 20%.

Figure 4 summarizes the results of the most recent temperature dependent studies of the rate constant of reaction (1) and shows an exceptional agreement (within 10% at T < 400 K) between rate constants reported by several research groups [5-7,20-28]. One can note that the present results are in excellent agreement with the previous measurements of k_1. This can be considered as a validation of the new high temperature reactor and experimental approach used. The rate constant data from the present study can be represented as three parameter expression (in $cm^3molecule^{-1}s^{-1}$, red line in Fig. 4):

$$k_1 = 5.1\times10^{-17}\,T^{1.85}\,exp(-160/T) \text{ at } T = (230 - 898) \text{ K},$$

with estimated 20% uncertainty. Combining the present data with those from previous studies leads to the following expression (in $cm^3molecule^{-1}s^{-1}$, black solid line in Fig. 4):

$$k_1 = 2.64\times10^{-17}\,T^{1.93}\,exp(-114/T) \text{ at } T = (190 - 1300) \text{ K}$$

Reactions of OH with n-Pentane and n-Heptane

Reactions of OH radicals with n-pentane and n-heptane were studied using the protocol similar to that applied for reaction with propane. The range of concentrations of the alkanes at different temperatures of the study is shown in Tables II and III. The concentration of p-

cymene was monitored as a function of reaction time simultaneously with that of OH radical. The consumption of p-cymene was found to be negligible (less than 5%) despite the fact that in some experiments comparable concentrations of OH and p-cymene were used (Tables II and III). As it will be shown below, in these cases OH was consumed mainly on the wall of the reactor without an accompanying consumption of p-cymene.

Table II Reaction OH + n-Pentane: Summary of the Measurements of the Rate Constant

T (K)	Reactor Coating[a]	Number of Experiments	[Pentane] (10^{13} molecule cm^{-3})	α ($\Delta[OH]/\Delta[C_5H_{12}]$)[b]	k_2 (10^{-11} cm^3 molecule^{-1} s^{-1})[b]
248	HW	7	0.30-3.96	3.65	0.31
268	HW	7	0.68-8.33	1.58	0.33
300	HW	8	0.57-9.84	1.0	0.42
338	BA	6	0.09-1.94	3.63	0.46
343	HW	7	0.58-5.71	1.0	0.51
371	BA	6	0.49-6.60	1.85	0.55
419	BA	6	0.26-6.13	1.73	0.64
476	BA	6	0.54-4.63	1.49	0.74
562	BA	6	0.47-5.89	1.46	1.01
686	BA	6	0.58-4.64	1.29	1.46
733	BA	6	0.43-3.92	1.13	1.64
797	BA	6	0.40-4.26	1.0	2.03
900	BA	6	0.25-4.81	1.0	2.46

[a] HW: halocarbon wax; BA: boric acid.
[b] uncertainty on α and on k_2 is nearly 15 and 20%, respectively.

Table III Reaction OH + n-Heptane: Summary of the Measurements of the Rate Constant

T (K)	Reactor Coating[a]	Number of Experiments	[Heptane] (10^{13} molecule cm^{-3})	α ($\Delta[OH]/\Delta[C_7H_{16}]$)[b]	k_3 (10^{-11} cm^3 molecule^{-1} s^{-1})[b]
248	HW	5	0.09-0.37	23.4	0.54
268	HW	6	0.08-1.45	6.50	0.59
300	HW	6	0.24-4.66	2.20	0.67
338	BA	8	0.09-2.15	6.19	0.80
343	HW	8	0.32-3.81	1.0	0.86
375	BA	8	0.09-2.38	2.60	0.94
420	BA	7	0.20-3.83	2.0	1.11
476	BA	6	0.15-2.00	1.74	1.35
562	BA	6	0.34-2.40	1.58	1.57
686	BA	6	0.19-2.03	1.14	2.06
800	BA	7	0.27-4.85	1.0	2.68
896	BA	6	0.17-2.54	1.0	3.37

Figure 5 shows examples of pseudo-first order plots obtained from OH decay kinetics in reaction with n-pentane at T = 343 and 797 K in low and high temperature reactors coated with halocabon wax and boric acid, respectively. The corresponding rate constants determined from the slopes of the straight lines in Fig. 5 are shown in Table II.

The measurements of the rate constants of the reactions (2) and (3) as a function of temperature revealed an important contribution of the heterogeneous reaction of OH with surface adsorbed organics under certain experimental conditions. The heterogeneous complications were observed in both low and high temperature reactors and were more pronounced in the lower edge of the respective operative temperature ranges, where an abnormal and unexpected increase of the reaction rate constant with decreasing temperature was observed.
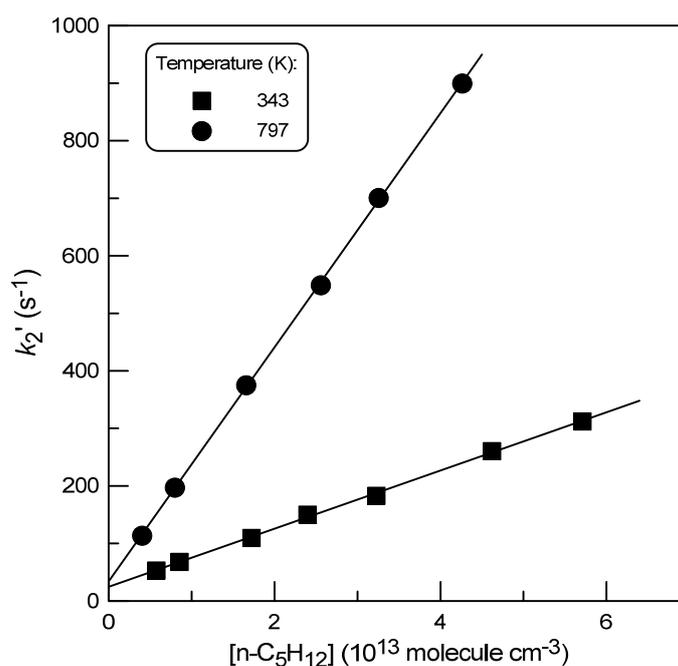

Figure 5 Reaction OH + n-C_5H_{12}: example of pseudo-first order plots obtained from OH decay kinetics at T = 343 and 797 K in reactors coated with halocabon wax and boric acid, respectively.

Direct evidence for the heterogeneous reaction is a dependence of the reaction rate on the type of the reactor surface. Figure 6 displays the pseudo-first order plots of OH consumption in reaction with n-heptane measured at fairly same temperature in the reactors coated with halocarbon wax and boric acid. The ratio of the slopes of two straight lines in Fig. 6 provides a factor of 5.73 for difference in the values of the reaction rate constant (k_3 =

0.86×10^{-11} and 4.93×10^{-11} $cm^3 molecule^{-1} s^{-1}$) measured under similar conditions in two reactors with different surface coating. It can be noted that we have not observed any indirect signs that usually accompany a heterogeneous reaction, such as the instability of the signals due to modification of the wall upon treatment with reactants and reaction products, poor reproducibility. For a given position of the injector, the concentrations of all species were stationary, not changing with time. The rates of wall loss of OH radicals measured in the absence of alkane in the reactor on "clean" surface and on that treated with alkanes were similar in the range of experimental uncertainty. Our experimental data do not allow to make any conclusion on the mechanism of the heterogeneous reaction. However, it can be noted that the linear dependence of the rate of the heterogeneous reaction on the gas phase concentration of heptane seems to indicate that a direct bimolecular reaction between OH radicals and n-heptane partitioned between gas phase and reactor surface (in the linear part of the Langmuir isotherm) is a limiting step of the heterogeneous interaction.

We have tried to use the fact that the dependence of the pseudo-first order rate constant on the concentration of alkane is linear, even under high contribution of the heterogeneous reaction, in order to make corrections for the heterogeneous chemistry and to extract the rate constants of the corresponding gas phase reactions.
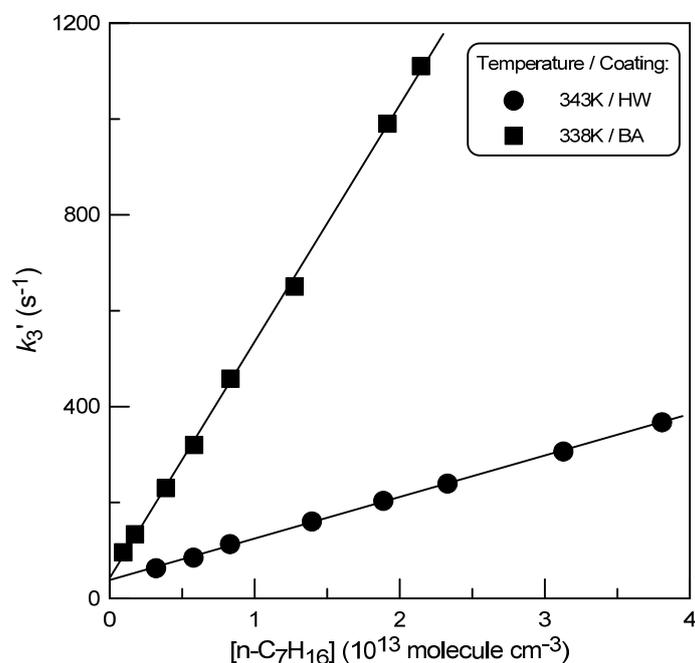

Figure 6 Reaction OH + n-C_7H_{16}: example of pseudo-first order plots obtained from OH decay kinetics at nearly 340 K in reactors coated with halocabon wax (HW) and boric acid (BA).

The rate of OH consumption in reaction with heptane can be expressed as:

$$d[OH]/dt = -k_{3measured} [OH][n\text{-}C_7H_{16}] = -\alpha \times k_3[OH][n\text{-}C_7H_{16}],$$

where correction factor α reflects the contribution of the heterogeneous reaction. Formally, and provided that the consumption of the organic compound on the reactor wall is negligible compared with the consumption of OH, this equation can be considered as corresponding to the following reaction:

$$\alpha \, OH + n\text{-}C_7H_{16} \rightarrow products,$$

where factor α represents the number of OH radicals consumed per one alkane molecule, and can therefore be determined experimentally. On this basis, at each temperature of the study, we have conducted additional experiments on the measurements of the ratio $\alpha = \Delta[OH]/\Delta[alkane]$. Experiments consisted in the successive titration of the same initial concentration of OH with an excess alkane and Br_2 (to measure the absolute concentration of OH) and the detection of the consumed fraction of these species. Example of the experimental results obtained at T = 338 K in the reactor coated with boric acid (corresponding to the kinetic data presented in Fig. 6) is shown in Fig. 7. The coefficient α can be easily determined as a ratio of the slopes of two straight lines in Fig.7 (corresponding to $\Delta[Br_2]$ and $\Delta[n\text{-}$heptane], respectively): $\Delta[OH]/\Delta[n\text{-}heptane]$ = 6.19. Dividing by this factor the rate constant determined from the data in Fig.6 at T = 338 K, 4.93×10^{-11} $cm^3 molecule^{-1}s^{-1}$, one gets the corrected for heterogeneous chemistry value of $k_3 = 0.80\times10^{-11}$ $cm^3 molecule^{-1}s^{-1}$, which is in excellent agreement with the value of 0.86×10^{-11} $cm^3 molecule^{-1}s^{-1}$, measured at T = 343 K in the halocarbon wax coated reactor under negligible contribution of the heterogeneous reaction. This procedure was applied for the measurements of the rate constants of the reactions of OH with n-pentane and n-heptane at all temperatures of the study. The corrective factors (α) and final values of the rate constants k_2 and k_3 are presented in Tables II and III. As one could expect, the contribution of the heterogeneous reaction increases with decrease of temperature, and is higher in the case of a heavier n-heptane molecule. Although the absolute values of the correction factors are, in a few cases, impressively high, the error on their determination, defined by the measurements of the consumed fractions of Br_2 and alkanes, was estimated to be within 15%, which leads to nearly 20% combined uncertainty on the measurements of k_2 and k_3.
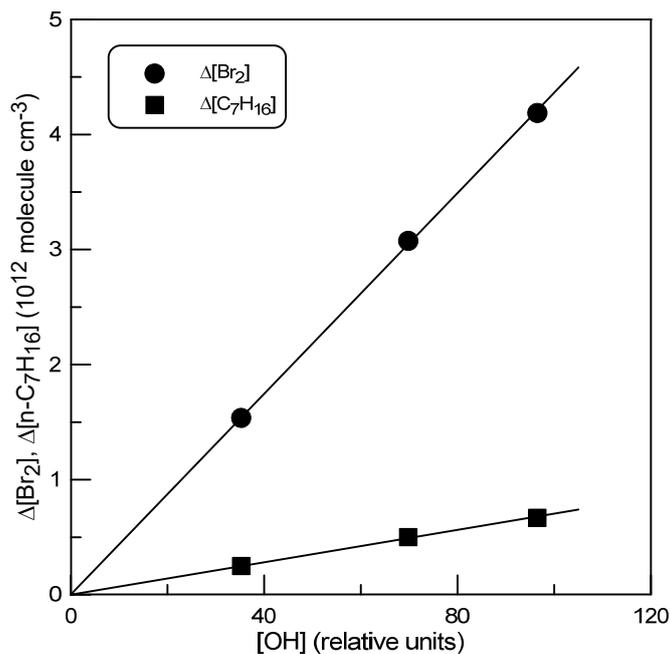
Figure 7 Concentrations of Br$_2$ and n-heptane consumed in reaction with OH as a function of consumed concentration of OH radicals: T = 338 K, boric acid coated reactor.

It should be noted again that the applied correction method implies that the consumption of alkane molecule on the wall of the flow reactor is negligible compared with that of OH radical. In the present work, this condition seems to be fulfilled, and correction procedure seems to be justified, as indicated by (i) the consistency of our results observed with different coatings of the flow reactor and (ii) by their good agreement with the rate constant data from previous studies (Fig. 8 and 9).
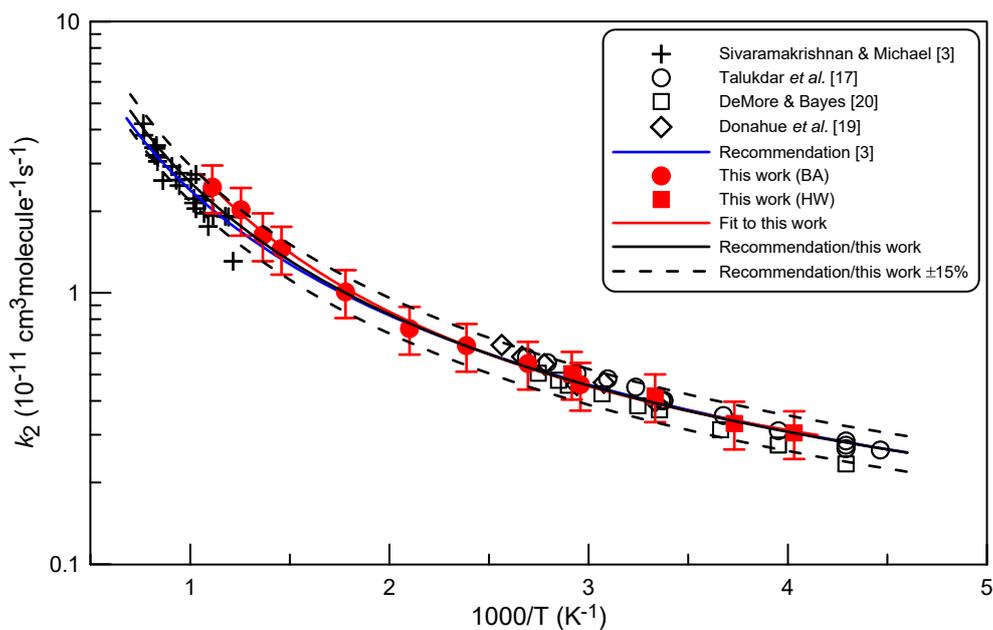
Figure 8 Reaction OH + n-pentane: summary of the measurements of the temperature dependence of the rate constant.
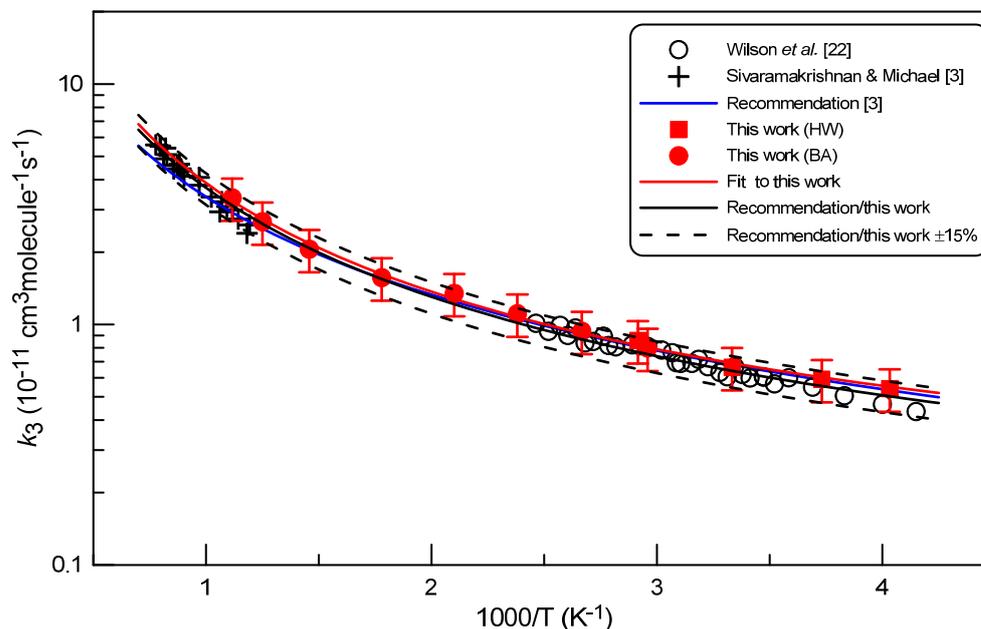

Figure 9 Reaction OH + n-heptane: summary of the measurements of the temperature dependence of the rate constant.

Figures 8 and 9 display the rate constants of the OH reactions with n-pentane and n-heptane measured in the present study together with those from the previous temperature dependent measurements [8,24,26,27,29]. For both reactions, our data, being in good agreement (within experimental uncertainty) with previous low (< 400 K) and high temperature (> 800 K) measurements, fill the gap in the kinetic database between 400 and 800 K. The rate constants of the reactions of OH with n-pentane and n-heptane measured in the present study can be represented as three parameter expressions (in $cm^3 molecule^{-1} s^{-1}$, red lines in Fig. 8 and 9):

$k_2 = 5.8 \times 10^{-18} T^{2.2} \exp(260/T)$ at T = (248 – 900) K,

$k_3 = 2.7 \times 10^{-16} T^{1.7} \exp(138/T)$ at T = (248 - 896) K

with estimated 20% uncertainty on k_2 and k_3. Combining the present data with those from previous studies the following expressions for k_2 and k_3 can be recommended from this work (in $cm^3 molecule^{-1} s^{-1}$, black solid lines in Fig. 8 and 9) :

$k_2 = 9.0 \times 10^{-17} T^{1.8} \exp(120/T)$ at T = (220 – 1300) K

$k_3 = 3.75 \times 10^{-16} T^{1.65} \exp(101/T)$ at T = (240 - 1300) K,

The dashed lines in Fig. 8 and 9 correspond to ±15% deviations from these equations showing that practically all existing data fall into this range.

CONCLUSION

In this work, we presented a newly developed low pressure (a few Torr) flow reactor, which in combination with a modulated molecular beam mass spectrometer, allows the measurements of the rate constants of the reactions of OH radicals at temperatures up to 1000 K. The temperature dependence of the rate constant of the reaction of OH with propane measured at T = (230-898) K was found to be in excellent agreement with multiple previous data for this well-studied reaction, that can be considered as a validation of the experimental approach and equipment. The rate constants of the reactions of OH radicals with n-pentane and n-heptane were measured in the temperature ranges 248-900K and 248-896 K, respectively, allowing to address the lack of the kinetic data in the temperature range between 400 and 800 K.

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