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# Absolute and relative rate constants for the reactions of OH and Cl with Pentanols

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**ABSTRACT**

The rate constants for the reactions of OH with three pentanols have been determined in the range 267-373 K and P=100 Torr. The data obtained were (in units of $cm^3molecule^{-1}s^{-1}$): k(1-pentanol) = $(6.7 \pm 3.8)\times10^{-12}$ exp [(132±176)/T], k(2-pentanol) = $(5.2 \pm 1.8)\times10^{-12}$ exp [(218±116)/T], k(3-pentanol) = $(5.8 \pm 2.3)\times10^{-12}$ exp [(164±118)/T]. The present work provides the first temperature dependence data on these reactions. In addition, using the relative rate method, the rate constants for OH and Cl with these pentanols have been measured. The results are compared with the literature data and discussed with respect to atmospheric chemistry.

Keywords: OH radicals, Cl atoms, 1-pentanol, 2-pentanol, 3-pentanol.

## 1. Introduction

Alcohols are an important class of oxygenated volatile organic compounds; their presence in ambient air is due to both natural and anthropogenic sources [e.g. 1, 2]. They are emitted by grassland and agricultural vegetation and have long been used as industrial solvents as well as motor vehicle fuels and fuel additives. Their oxidation in the atmosphere produces wide variety of carbonyls such as aldehydes and ketones as major reactions products followed by the formation of nitro-containing compounds and other photooxidants which could be more toxic with higher impact on air quality than the initial alcohols [e.g. 2, 3]. Thus, alcohols have a potential to contribute to the adverse effects that are caused by anthropogenic organic air pollutants such as photooxidants formation.

It is well established that the atmospheric oxidation in the gas phase of saturated organic compounds such as those investigated in the present study is mainly controlled by reaction with hydroxyl radicals; reactions with other oxidants such as ozone and nitrate radicals being of minor importance. Sunlight initiated photolysis is also a negligible process for compounds such as saturated alcohols [e.g. 3, 4]. However, chlorine atoms initiated oxidation of organics may play an important role because this later process may exert some influence in the boundary layer, particularly in marine and coastal environments [e.g. 5] and some urban regions [6]. Therefore, in order to quantify the contribution of alcohols to the photooxidants formation in the troposphere, it is of importance to understand the kinetics and mechanisms of their OH- and Cl-initiated oxidation.

In the present work, we have measured the rate constants for the reactions of OH radicals and Cl atoms with three pentanols: 1-pentanol ($CH_3(CH_2)_3CH_2OH$), 2-pentanol ($CH_3(CH_2)_2CH(OH)CH_3$) and 3-pentanol ($CH_3CH_2CH(OH)CH_2CH_3$):

OH/Cl + 1-pentanol ($CH_3CH_2CH_2CH_2CH_2OH$) → products (1/4)

OH/Cl + 2-pentanol ($CH_3CH_2CH_2CH(OH)CH_3$) → products (2/5)

OH/Cl + 3-pentanol ($CH_3CH_2CH(OH)CH_2CH_2OH$) → products (3/6)

Using the pulsed laser photolysis-laser induced fluorescence as absolute technique, the rate constants for the OH reactions have been determined in the temperature range 267-373 K. The measurements have been also conducted using a relative method to investigate the reactivity of both OH and Cl with the three pentanols at room temperature. This work provides the first temperature dependence investigation for the OH reactions with pentanols. Among the reactions investigated here, the reaction of OH with 1-pentanol is the most documented, it has been studied previously by Wallington and Kurylo [7] using flash photolysis-resonance fluorescence technique and by several groups using the relative rate method [8-11]. Nelson et al. have also reported a study using the pulsed radiolysis-UV absorption method [8]. The other reactions have been investigated previously only once or twice (besides Cl reaction with 1-pentanol which has been studied by three groups) [8, 11-16]. The kinetic data obtained in this work are compared with the previous studies and discussed in terms of the atmospheric implications.

## 2. Experimental

The pulsed laser photolysis – laser induced fluorescence (PLP-LIF) technique has been used to investigate the temperature dependence of the OH reactions with pentanols at around 100 Torr of helium. The relative rate method was used to measure the rate constants for OH and Cl reactions with the same pentanols at T = (298 ± 2)K and P=760 Torr of air.

### *2.1. Absolute rate measurements*

The PLP-LIF system as well as the methodology used to derive the kinetic parameters has been described in details in previous papers from our group [e.g. 17]. Hence, only a brief presentation is given here. Photolysis of $H_2O_2$ at λ=248 nm using an excimer laser was used as OH source. The hydroxyl radical concentration was then monitored by laser induced fluorescence at various reaction times. A Nd:YAG pumped frequency doubled-dye laser was used to excite OH at λ≈282 nm and its fluorescence was detected at λ≈309 nm using a photomultiplier fitted with a narrow band-pass filter. The reaction cell made of Pyrex was heated or cooled by circulating heated water or cooled ethanol through a double jacket. The temperatures as well as the total pressure were measured in the center of the reaction cell.

All experiments were carried out under pseudo-first-order conditions with $[pentanol]_0 >> [OH]_0$. Under these conditions, the temporal profiles of [OH] followed the pseudo-first-order rate law:

$$[OH]_t = [OH]_0 \exp(-k't) \qquad \text{where } k' = k_i\,[pentanol] + k_0'$$

Where $k_i$ represents the rate constants for the reaction of OH radical with the studied alcohols and $k_0'$ is the first-order OH decay rate in absence of alcohols. $k_i$, the bimolecular rate constant for the reaction of pentanols with OH, is obtained from the slope of the plot k' vs. [pentanol]. The concentrations of the alcohols were determined from the mass flow rates, temperature and pressure in the cell. The alcohols were premixed with helium (0.13-0.80)% in a 10 liters glass bulb at a total pressure of 800-900 Torr. The gas mixtures containing pentanols, hydrogen peroxide and helium were flowed through the cell with a linear velocity ranging from 5 to 20 $cm^{-1}$.

*2.2. Relative rate measurements*

This method was used to measure the rate constants for both Cl and OH reactions with pentanols at 298 ± 2 K and 760 Torr of purified air in a 140 L Teflon bag reaction chamber. The experimental set-up has been described previously [e.g. 18]. The reaction chamber is surrounded by banks of fluorescent lamps, six of them providing radiation at 254 nm (Philips TUV, 15W) used to produce OH radicals through the photolysis of $H_2O_2$ and six other black lamps (Philips, TL 20W/05) with a maximum irradiation at 365 nm used to generate Cl atoms by photolysing $Cl_2$. Measured amounts of reactants were expanded into the evacuated vacuum line and isolated into a calibrated mixing bulb, from which they were swept into the reaction chamber by a stream of zero-grade air. The chamber was then filled to its full capacity at atmospheric pressure with ultra-pure air. A gas chromatograph-flame ionization detector (GC-

FID, Star 3800 CX, Varian) was used for the quantitative analysis of the reactants. Chromatographic separation was achieved by using a DB-1 capillary column (J&W Scientific, 30 m, 0.25 id, 5 μm film).

Relative rate constants for the reactions of OH radicals and Cl atoms with the three pentanols were determined by comparing their rates of decay with reference compounds whose rate constants have been previously established. In the presence of OH radicals or chlorine atoms the pentanol and reference compounds decay due reactions I and II.

$$\text{OH/Cl} + \text{pentanol} \rightarrow \text{products} \qquad \text{(I)}$$

$$\text{OH/Cl} + \text{reference} \rightarrow \text{products} \qquad \text{(II)}$$

Provided that both substrate and reference are only lost by reaction with OH radicals or Cl atoms, neither organic is reformed in any process, and the dilution due to sampling is negligible, it can be shown that

$$\ln([\text{pentanol}]_0/[\text{pentanol}]_t) = (k_{pent}/ k_{ref}) \ln([\text{reference}]_0/[\text{reference}]_t) \qquad \text{(III)}$$

where the subscripts 0 and t indicate concentrations at the start of the reaction and at time t, respectively. $k_{pent}$ is the second-order rate constants for the reactions of OH or Cl with the studied alcohols, likewise $k_{ref}$ is that for the reaction of OH or Cl with the reference compounds. Thus, plot of $\ln([\text{pentanol}]_0/[\text{pentanol}]_t)$ vs. $\ln([\text{reference}]_0/[\text{reference}]_t)$ should be straight line passing through the origin, whose slope gives the ratio of rate constants $k_{pent}/k_{ref}$.

Materials: The purities of the chemicals were as follows: Helium, UHP certified to >99.9995%, (Alphagaz); $N_2$-$O_2$ (80-20), certified to >99.995%; chlorine, 99.8 % (UCAR); 1-pentanol, >99% (Fluka); 2-pentanol, 99% (Alfa Aesar); 3-pentanol >98% (Alfa Aesar), cyclohexane, 99.5% (Riedel); 1,3-dioxane, >99% (Fluka); pentane, >99.5% (Aldrich).

## 3. Results and discusion

### *3.1. Relative rate measurements*

The pentanols and the reference compounds employed were shown to be stable in the dark and their photolytic loss was found to be negligible over the time period of the kinetic experiments. The initial concentration of the alcohols and references were in the range 30-110 ppm for OH reactions and 36-183 ppm for the Cl experiments. $H_2O_2$ and $Cl_2$ were in the range 20-200 ppm. Two individual runs were carried out for each of the pentanols with a particular reference compound. Figure 1 shows examples of experimental plots derived from the analysis of a relative rate measurement for the reactions of alcohols with OH and Cl, respectively. As expected, straight lines with a zero intercept were obtained, showing in all cases a good linearity. The rate constants of the reactions of 1-pentanol, 2-pentanol and 3-pentanol with OH radicals and Cl atoms at T= (298±2) K and P = 760 Torr obtained using the relative rate method, are summarized in Table I. The measured rate constant ratios were placed on an absolute scale using pentane, 1,3-dioxolane and cyclohexane as reference compounds. The reference reactions rate constants values used are (in $cm^3$ $molecule^{-1}$ $s^{-1}$):

k(OH+pentane) = (3.92 ± 0.17)×$10^{-12}$, k(Cl+pentane) = (2.7 ± 0.4) ×$10^{-10}$ [19], k(OH+1,3-dioxolane) = (1.0 ± 0.35) ×$10^{-11}$, k(Cl+1,3-dioxolane) = (1.65 ± 0.25) ×$10^{-10}$ [2], k(OH+cyclohexane) = (6.97 ± 1.39) ×$10^{-12}$ [19], k(Cl+cyclohexane) = (3.3 ± 0.5) ×$10^{-10}$ [19]. The rate constants for the reactions were derived by averaging the values from different experiments with error limits that encompass the extremes of σ error of the individual determinations and do not include systematic errors and uncertainties of the reference rate constants which could be as high as 30% are the following:

| Alcohols | k(OH) | k(Cl) |
|---|---|---|
| | ($cm^3$ $molecule^{-1}$ $s^{-1}$) | ($cm^3$ $molecule^{-1}$ $s^{-1}$) |
| 1-pentanol ($CH_3(CH_2)_3CH_2OH$) | (1.0±0.1)×$10^{-11}$ | (2.9±0.2)×$10^{-10}$ |
| 2-pentanol ($CH_3(CH_2)_2CH(OH)CH_3$) | (1.1±0.1)×$10^{-11}$ | (2.1±0.2)×$10^{-10}$ |
| 3-pentanol ($CH_3CH_2CH(OH)CH_2CH_3$) | (1.1±0.1)×$10^{-11}$ | (2.2±0.1)×$10^{-10}$ |

*3.2. Absolute rate measurement*

The rate constants $k_1$-$k_3$ were measured under pseudo first order conditions where the concentrations of pentanols were in the range 0.5-20, 1.4-58 and 2-78 (in $10^{13}$ molecule $cm^{-3}$) for 1-pentanol, 2-pentanol and 3-pentanol, respectively, while the concentrations of OH radicals were typically around 3×$10^{11}$ molecule $cm^{-3}$. Variation in the experimental conditions such as the flow velocity and laser fluence did not affect the results. The experiments were

conducted at a total pressure of 100 Torr of helium. The experimental conditions and the results obtained are summarized in Table II. Figure 2 displays examples of the plots of ($k'$-$k_0$) versus pentanol concentrations from which the rate constants were derived at T=298K. Figures 3-5 show the data in the Arrhenius forms (k vs. 1000/T) from which the Arrhenius parameters are derived. The quoted errors for the rate constants determined here include $2\sigma$ from the least squares analysis and an estimated error due mainly to the measurement of the concentrations, estimated to 5%. The uncertainties for the Arrhenius parameters A and E/R are given by $\delta A = 2A\sigma_{lnA}$ and $\delta(E/R) = 2\sigma_{E/R}$, respectively.

The Arrhenius expressions obtained in the temperature range 273-373 K for $k_1$ and $k_2$ are:

$$k_1 = (6.7 \pm 3.8)\times10^{-12} \exp[(132\pm176)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (5.2 \pm 1.8)\times10^{-12} \exp[(218\pm116)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and for $k_3$, studied in the temperature range 267-373 K:

$$k_3 = (5.8 \pm 2.3)\times10^{-12} \exp[(164\pm118)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The rate constant values derived at T = 298 K are (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_1 = (1.0\pm 0.1)\times10^{-11}$, $k_2 = (1.0 \pm 0.1)\times10^{-11}$ and $k_3 = (1.0 \pm 0.1)\times10^{-11}$.

*3.3. Discussion*

The rate constants for the reactions of OH with the investigated pentanols at 298 K obtained in this work using both absolute and relative rate methods are in very good agreement, within 10 %. The rate constants obtained in this study are compared with the previously reported

data in Table III. The previous investigations have been conducted mainly using the relative rate methods, the only absolute technique studies are those by Wallington et al. (1987, 1988) for the three alcohols and Nelson et al. (1990) for 1-pentanol. For the previous relative rate method studies, we have used the recommended or preferred values for the rate constants of the reactions of OH with the reference compounds in the same manner as Calvert et al. [2] to recalculate the rate constants values.

As shown in Table III, the rate constants data for the reaction of OH with 1-pentanol from different measurements at T ≈ 298 K are in good agreement disregarding the one from Oh and Andino (2001) where they used p-xylene as the reference compound (≈30% higher than the other measurements).

The reactions of OH with 2-pentanol and 3-pentanol have been each investigated only twice as shown in Table III. Wallington et al. (1988) used the flash photolysis-resonance fluorescence technique and Baxley and Wells (1998) used the relative rate method and GC as analytical tool to determine the rate constant for the reaction of OH with 2-pentanol. Hurley et al. (2008) measured k(OH+3-pentanol) using also a relative rate technique but with FTIR as analytical method. All investigations were conducted at T ≈ 298K. The values derived in the present work are in good agreement with these previous studies for both reactions. The present work provides the first temperature dependence studies of the rate constants for the reactions of OH with three pentanols.

The values obtained here for the reactions of Cl atoms with pentanols are also in good agreement with the previously determined ones as shown in Table III. While the reaction of Cl with 1-pentanol has been studied by three other groups, this work provides the second determinations for k(Cl+2-pentanol) and k(Cl+3-pentanol) at room temperature. The only temperature dependence study on these reactions available so far is that performed by Garzón et al. (2006) in the temperature range T = (264-381) K for the reaction of Cl with 1-pentanol: k(Cl+1-pentanol)= $(3.97\pm0.48)\times10^{-11}$ exp[(533±77)/T] $cm^3$ $mocule^{-1}$ $s^{-1}$.

The rate constants values for OH reactions with the three pentanols investigated in the present study are similar within the reported uncertainties k(OH+pentanol) ≈ $(1.15\pm0.15)\times10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ indicating that the position of the hydroxyl group (-OH) in these species does not affect their reactivity toward OH radicals. To the best of our knowledge, there are no available mechanistic studies on the reaction of OH with pentanols. However, using the structure-activity relationship (SAR), one can predict the contribution of each reactive site to the overall reaction and hence the reactions products [20, 21]. The available literature data indicate that the reaction occurs mainly through the H-atom abstraction from $CH_x$ groups (x=1 or 2) at the α- and β-positions to the –OH group and to a lesser extent at the other positions.

From the SAR predictions and the available studies on other oxygenated compounds, the expected major oxidation products under atmospheric conditions are the corresponding carbonyls: pentanal for 1-pentanol, 2-pentanone for 2-pentanol, and 3-pentanone for 3-

pentanol in addition to shorter ketones and aldehydes (butanal, butanone, propanone, propanal, acetone and acetaldehyde, …).

## 4. Atmospheric implications

Alcohols are removed from the atmosphere mainly through gas phase reactions with OH radicals and Cl atoms. Other gas phase chemical processes such as reactions with $O_3$ and $NO_3$ are expected to be negligible. Similarly, photolysis is not an important atmospheric loss process for the alcohols since they do not absorb solar radiation at actinic wavelengths. Thus, the tropospheric lifetimes can be estimated using the kinetic parameters derived in this work along with the concentrations of OH radicals and Cl atoms. Taking the tropospheric concentration of OH radicals to be 1 x $10^6$ radicals $cm^{-3}$ (24 h daytime average) and that of Cl atoms to be 1 x $10^3$ atoms $cm^{-3}$ (24 h average), the calculated lifetimes ($\tau=1/k[X]$ with X=OH and Cl) are around one day and 3 months against the reactions with OH and Cl, respectively. However, it has to be mentioned that in some specific areas such as marine or coastal regions, the concentrations of Cl atoms can be much higher than that used here which will shorter the lifetimes of the alcohols and other organic compounds and make the reaction with Cl the most dominant removal process of these species in these regions.

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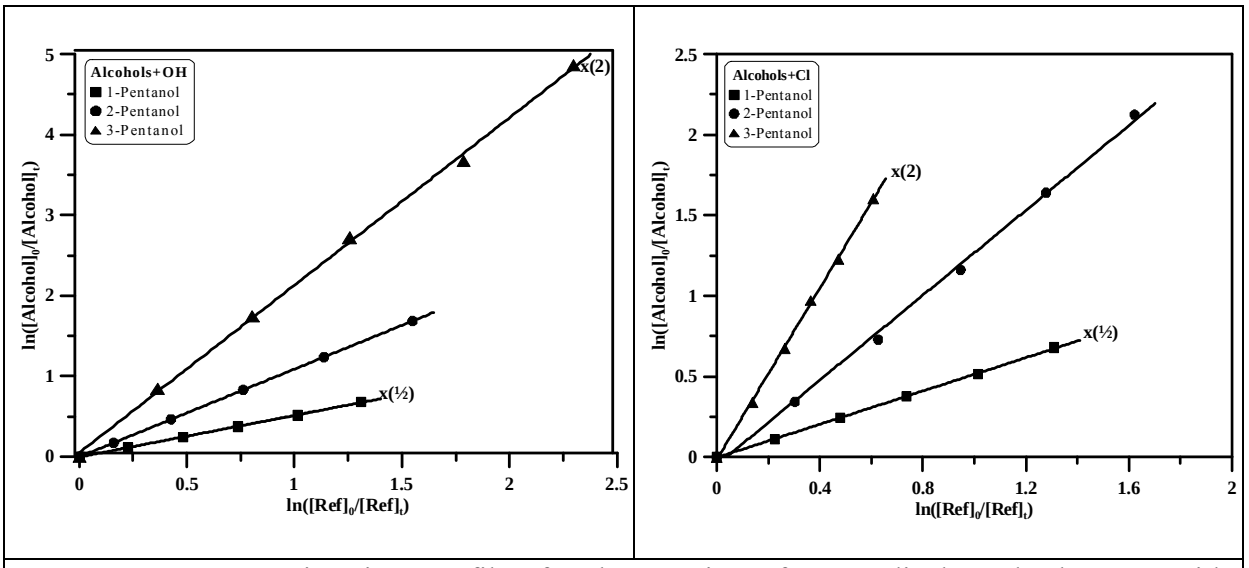


**Figure 1**. Concentration-time profiles for the reaction of OH radicals and Cl atoms with pentanols using 1,3-dioxolane as reference compound at 298±2 K and atmospheric pressure.

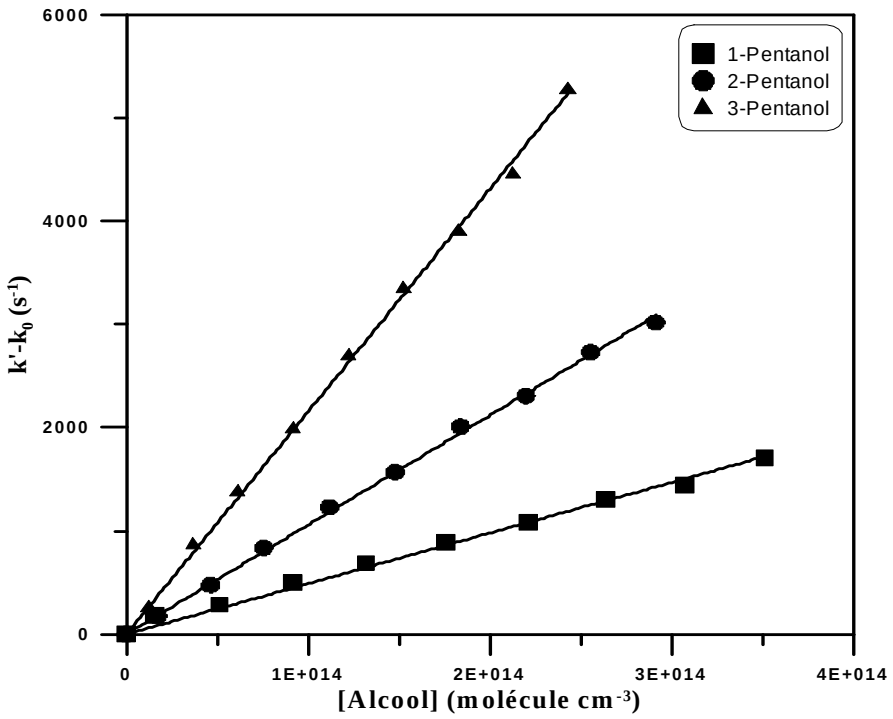


**Figure 2**. Reactions OH + pentanols: plots of k'-$k_0$ vs. pentanols concentration at T=(298 ±1)K. The lines represent the linear squares fittings.

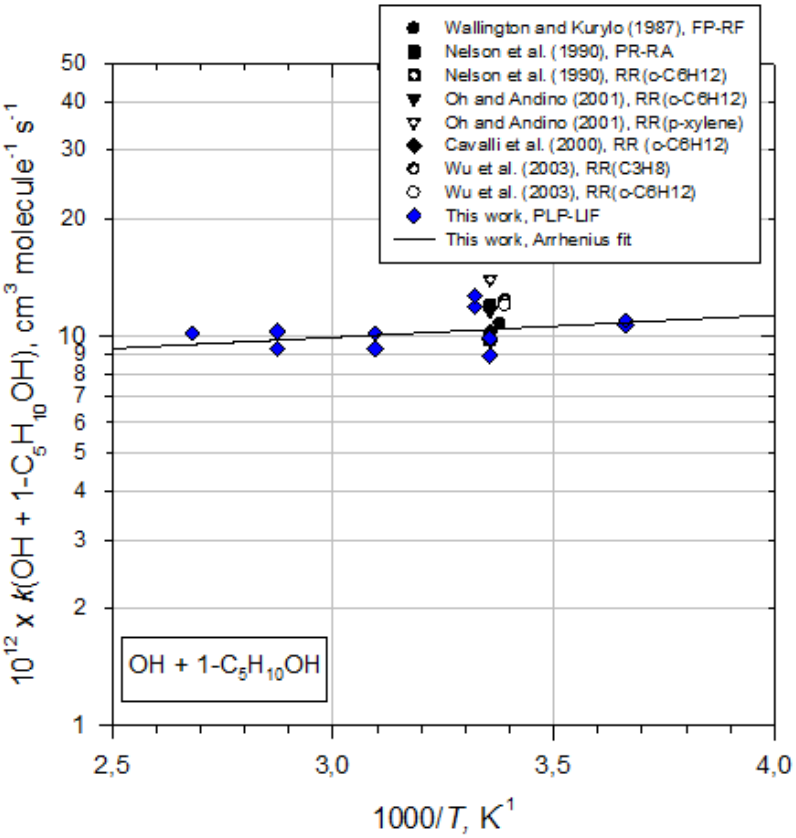


**Figure 3**. Plots of $k_1$ as function of 1000/T for the OH reaction with 1-Pentanol

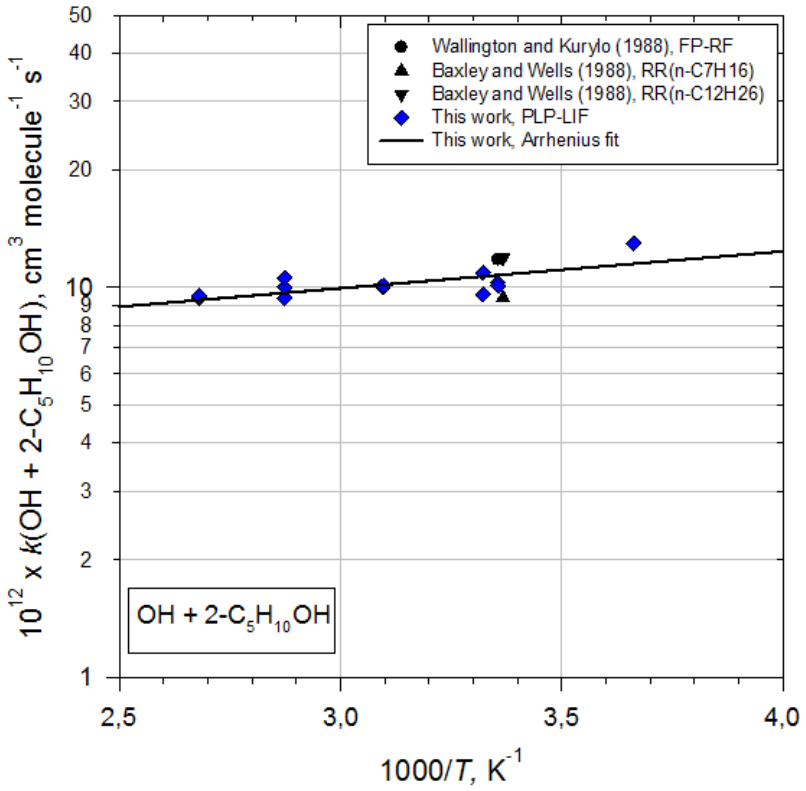


**Figure 4**. Plots of $k_2$ as function of 1000/T for the OH reaction with 2-Pentanol

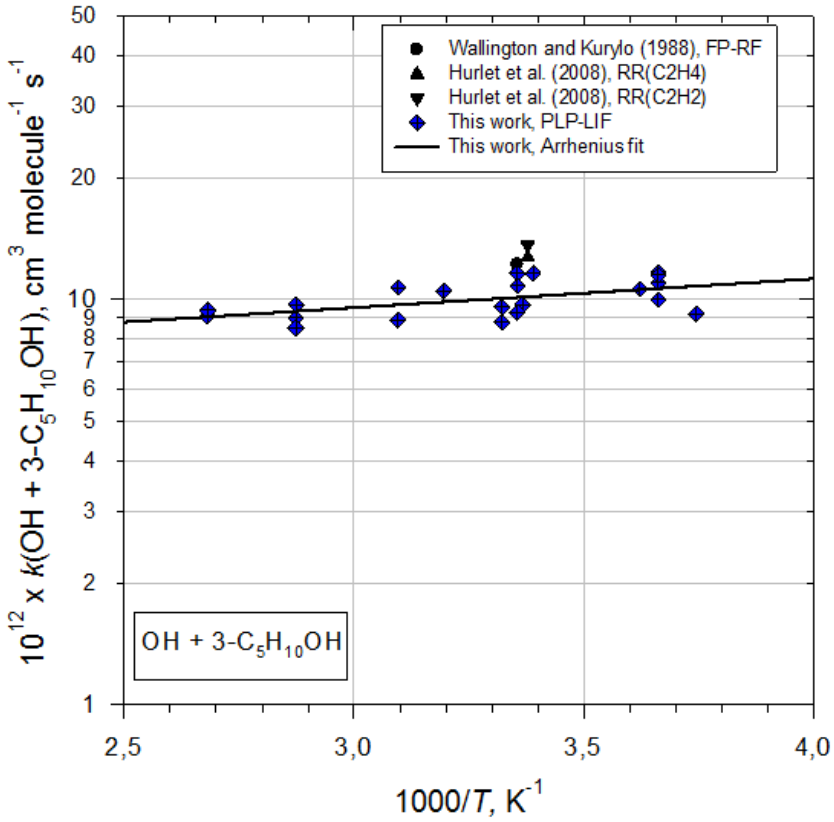


**Figure 5**. Plots of $k_3$ as function of 1000/T for the OH reaction with 3-Pentanol

**Table I.** Reactant concentrations and slopes, $k_{alcohol}/k_{ref}$, and the obtained rate constant for the reaction of OH and Cl with alcohols at 298±2 K and atmospheric pressure.

| Alcohol | Reference | Number of runs | $k_{alcohol}/k_{ref}$ [a] | $k_{alcohol}$ [b] |
|---|---|---|---|---|
| | | **OH reactions** | | |
| 1-Pentanol | Cyclohexane | 2 | 1.43±0.07 | $0.99 \times 10^{-11}$ |
| | 1.3-dioxolane | 2 | 1.04±0.02 | $1.04 \times 10^{-11}$ |
| | | Average | | $(1.0 \pm 0.1)\times10^{-11}$ |
| 2-Pentanol | Pentane | 2 | 3.14±0.15 | $1.22 \times 10^{-11}$ |
| | 1.3-dioxolane | 2 | 1.08±0.01 | $1.08 \times 10^{-11}$ |
| | | Average | | $(1.1 \pm 0.1)\times10^{-11}$ |
| 3-Pentanol | Pentane | 2 | 3.05±0.18 | $1.19 \times 10^{-11}$ |
| | 1.3-dioxolane | 3 | 1.05±0.03 | $1.05 \times 10^{-11}$ |
| | | Average | | $(1.1 \pm 0.1)\times10^{-11}$ |
| | | **Cl reactions** | | |
| 1-Pentanol | Cyclohexane | 3 | 0.93±0.02 | $3.07 \times 10^{-10}$ |
| | 1.3-dioxolane | 3 | 1.65±0.16 | $2.72 \times 10^{-10}$ |
| | | Average | | $(2.9 \pm 0.2)\times10^{-10}$ |
| 2-Pentanol | Pentane | 2 | 0.82±0.06 | $2.21 \times 10^{-10}$ |
| | 1.3-dioxolane | 2 | 1.22±0.10 | $2.01 \times 10^{-10}$ |
| | | Average | | $(2.1 \pm 0.2)\times10^{-10}$ |
| 3-Pentanol | Pentane | 2 | 0.82±0.09 | $2.21 \times 10^{-10}$ |
| | 1.3-dioxolane | 2 | 1.29±0.08 | $2.16 \times 10^{-10}$ |
| | | Average | | $(2.2 \pm 0.1)\times10^{-10}$ |

[a] The errors quoted for the $k_{alcohol}/k_{ref}$ values are twice the standard deviation arising from the least-squares fit of the straight lines and do not include the corresponding statistical error in the reference rate constant.

[b] Units of $cm^3$ $molecule^{-1}$ $s^{-1}$.

**Table II.** Reactions OH + Pentanols: summary of experimental conditions and measured rate constants.

| T (K) | [1-Pentanol] ($\times 10^{13}$)[a] | ($k_1 \pm 2\sigma$)[b] $\times 10^{11}$ | [2-Pentanol] ($\times 10^{13}$)[a] | ($k_2 \pm 2\sigma$)[b] $\times 10^{11}$ | [3-Pentanol] ($\times 10^{13}$)[a] | ($k_3 \pm 2\sigma$)[b] $\times 10^{11}$ |
|---|---|---|---|---|---|---|
| 267 | | | | | 3.20-77.5 | 0.90 ± 0.09 |
| 273 | 0.72-16.2 | 1.05 ± 0.04 | 1.41-16.2 | 1.26 ± 0.09 | 2.33-26.6 | 1.10 ± 0.09 |
| 273 | 0.89-9.43 | 1.04 ± 0.13 | | | 3.06-67.4 | 1.07 ± 0.07 |
| 273 | | | | | 2.91-49.9 | 1.09 ± 0.09 |
| 273 | | | | | 3.35-37.9 | 1.11 ± 0.10 |
| 276 | | | | | 3.27-74.4 | 1.03 ± 0.03 |
| 295 | | | | | 3.59-70.6 | 1.16 ± 0.03 |
| 297 | | | | | 2.87-62.2 | 0.95 ± 0.05 |
| 298 | 0.79-17.6 | 0.93 ± 0.04 | 1.71-32.7 | 1.00 ± 0.07 | 2.76-67.4 | 1.13 ± 0.02 |
| 298 | 0.67-16.6 | 0.97 ± 0.02 | 1.98-49.1 | 0.94 ± 0.12 | 3.56-70.1 | 0.91 ± 0.04 |
| 298 | 0.78-19.4 | 0.84 ± 0.04 | | | 2.45-54.4 | 1.07 ± 0.02 |
| 301 | 0.75-19.1 | 1.19 ± 0.11 | 2.06-52.8 | 1.06 ± 0.11 | 2.68-67.8 | 0.96 ± 0.03 |
| 301 | 0.76-19.5 | 1.24 ± 0.12 | 2.26-57.7 | 0.92 ± 0.06 | 2.73-67.5 | 0.81 ± 0.08 |
| 313 | | | | | 3.12-66.1 | 1.03 ± 0.05 |
| 323 | 0.70-17.9 | 0.99 ± 0.05 | 1.59-30.3 | 0.99 ± 0.01 | 2.52-63.6 | 0.82 ± 0.06 |
| 323 | 0.62-15.5 | 0.90 ± 0.03 | 1.94-49.4 | 1.00 ± 0.05 | 2.76-56.3 | 1.08 ± 0.05 |
| 348 | 0.66-16.8 | 1.03 ± 0.02 | 1.73-42.5 | 1.01 ± 0.01 | 2.31-58.9 | 0.87 ± 0.09 |
| 348 | 0.57-14.1 | 0.91 ± 0.02 | 1.78-45.4 | 1.04 ± 0.06 | 2.41-58.1 | 0.96 ± 0.02 |
| 348 | | | | | 2.30-58.8 | 0.83 ± 0.04 |
| 373 | 0.62-15.7 | 0.99 ± 0.07 | 1.40-26.8 | 0.94 ± 0.02 | 2.15-54.9 | 0.87 ± 0.04 |
| 373 | 0.52-11.8 | 0.87 ± 0.03 | 1.66-42.6 | 0.92 ± 0.07 | 2.46-54.5 | 0.93 ± 0.04 |

[a] Units of molecule $cm^{-3}$. [b] Units of $cm^3$ $molecule^{-1}$ $s^{-1}$.

**Table III.** Comparison of OH and Cl reaction rate constants with previous work.

| Alcohol | T (K) | k, [a, b] ($\times10^{-11}$) | A,[a] ($\times10^{-12}$) | E/R, K | ΔT (K) | Technique[d] | Ref |
|---|---|---|---|---|---|---|---|
| | **OH reaction** | | | | | | |
| **1-Pentanol** | 298±2 | 1.0±0.1 | 6.7±3.8 | -(132±176) | 273-373 | PLP-LIF | This work |
| | 298±3 | 1.0±0.1 | | | | RR | This work |
| | 296 | 1.08±0.11 | | | | FP-RF | [7] |
| | 298±2 | 1.20±0.16 | | | | PR-UVabs | [8] |
| | | 0.98±0.12 | | | | RR(c-$C_6H_{12}$) | [8] |
| | 298 | 1.03±0.11 | | | | RR(c-$C_6H_{12}$) | [9] |
| | 298±2 | 1.16±0.06 | | | | RR(c-$C_6H_{12}$) | [10] |
| | | 1.40±0.07 | | | | RR(p-xylene) | [10] |
| | 295±2 | 1.24±0.10 | | | | RR($C_3H_8$) | [11] |
| | | 1.20±0.05 | | | | RR(c-$C_6H_{12}$) | [11] |
| **2-Pentanol** | 298±2 | 1.0±0.1 | 5.2±1.8 | -(218±116) | 273-373 | PLP-LIF | This work |
| | 298±3 | 1.1±0.1 | | | | RR | This work |
| | 298 | 1.18±0.08 | | | | FP-RF | [12] |
| | 297±3 | 0.94±0.11 | | | | RR(n-$C_7H_{16}$) | [13] |
| | 297±3 | 1.19±0.08 | | | | RR(n-$C_{12}H_{26}$) | [13] |
| **3-Pentanol** | 298±2 | 1.0±0.1 | 5.8±2.3 | -(164±118) | 273-373 | PLP-LIF | This work |
| | 298±3 | 1.1±0.1 | | | | RR | This work |
| | 298 | 1.22±0.07 | | | | FP-RF | [12] |
| | 296±2 | 1.27±0.12 | | | | RR($C_2H_4$) | [14] |
| | 296±2 | 1.36±0.15 | | | | RR($C_3H_6$) | [14] |
| | **Cl reaction** | | | | | | |
| | T (K) | k, [a, b] ($\times10^{-10}$) | A,[a] ($\times10^{-11}$) | E/R, K | ΔT (K) | Technique[c] | Ref |
| **1-Pentanol** | 298±2 | 2.9±0.2 | | | | RR | This work |
| | 298±2 | 2.63±0.14 | | | | RR(c-$C_6H_{12}$) | [8] |
| | 298±2 | 2.75±0.27 | | | | RR($C_3H_8$) | [11] |
| | 298±2 | 2.77±0.13 | | | | RR(c-$C_6H_{12}$) | [11] |
| | 298±2 | 2.37±0.29 | 3.97±0.48 | -(533±77) | 264-381 | PLP-RF | [15] |
| **2-Pentanol** | 298±3 | 2.1±0.2 | | | | RR | This work |
| | 298±2 | 2.18±0.36 | | | | RR(1,3-butadiene) | [16] |
| **3-Pentanol** | 298±3 | 2.2±0.1 | | | | RR | This work |
| | 296±2 | 2.1±0.2 | | | | RR($C_2H_4$) | [14] |
| | 296±2 | 1.8±0.2 | | | | RR($C_3H_6$) | [14] |

[a] Units of $cm^3$ $molecule^{-1}$ $s^{-1}$.

[b] Placed on an absolute basis using k(c-$C_6H_{12}$) = $6.97\times10^{-12}$ [19]; k(p-xylene) = $1.43\times10^{-11}$ [22]; k($C_3H_8$) = $1.1\times10^{-12}$ [23]; k(n-$C_7H_{16}$) = $6.5\times10^{-12}$ [19]; = k(n-$C_{12}H_{26}$) = $1.36\times10^{-11}$ [19]; k($C_2H_4$) = $7.9\times10^{-12}$ [23] and k($C_3H_6$) = $2.9\times10^{-11}$ [23].

[c] Placed on an absolute basis using k(c-$C_6H_{12}$) = $3.3\times10^{-10}$ [19]; k($C_3H_8$) = $1.4\times10^{-10}$ [23]; k(1,3-butadiene) = $2.51\times10^{-10}$ [24]; k($C_2H_4$) = $9.5\times10^{-11}$ [2]; and k($C_3H_6$) = $2.3\times10^{-10}$ [23].

[d] Key: FP-RF, Flash Photolysis-Resonance Fluorescence; PLP-LIF, Pulsed Laser Photolysis-Laser Induced Fluorescence; PLP-RF, Pulsed Laser Photolysis- Resonance Fluorescence; RR, Relative Rate, PR-UVabs, Pulsed Radiolysis-UV absorption.