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Gas-phase Rate Coefficients for a Series of Alkyl Cyclohexanes with OH Radicals and Cl Atoms

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Abstract

The rate coefficients of the reactions of OH radicals and Cl atoms with three alkylcyclohexanes compounds, methylcyclohexane (MCH), trans 1,4-dimethylcyclohexane (DCH) and ethylcyclohexane (ECH) have been investigated at (293±1) K and 1000 mbar of air using relative rate methods. A majority of the experiments were performed in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC), a stainless steel chamber using in situ FTIR analysis and online GC-FID detection to monitor the decay of the alkylcyclohexanes and the reference compounds. The studies were undertaken to provide kinetic data for calibrations of radical detection techniques in HIRAC. The following rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}) were obtained for Cl reactions: $k_{(Cl+MCH)}=(3.51\pm\ 0.37)\times10^{-10}$, $k_{(Cl+DCH)}=(3.63\pm\ 0.38)\times10^{-10}$, $k_{(Cl+ECH)}=(3.88\pm 0.41)\times10^{-10}$ and for the reactions with OH radicals: $k_{(OH+MCH)}= (9.5\pm1.3)\times10^{-12}$, $k_{(OH+DCH)}=(12.1\ \pm\ 2.2)\times10^{-12}$, $k_{(OH+ECH)}=(11.8\ \pm\ 2.0)\times10^{-12}$. Errors are a combination of statistical errors in the relative rate ratio (2σ) and the error in the reference rate coefficient. Checks for possible systematic errors were made by the use of two reference compounds, two different measurement techniques, and also three different sources of OH were employed in this study; photolysis of CH_3ONO with black lamps, photolysis of H_2O_2 at 254 nm and non-photolytic trans-2-butene ozonolysis. For DCH some direct laser flash photolysis studies were also undertaken, producing results in good agreement with the relative rate measurements. Additionally, temperature dependent rate coefficient investigations were performed for the reaction of methylcyclohexane with OH radical over the range 273 K to 343 K using the relative rate method; the resulting recommended Arrhenius expression is $k_{(OH\ +\ MCH)} = (1.85 \pm 0.27) \times10^{-11} \exp((-1.62 \pm 0.16)\ kJ\ mol^{-1}/RT)\ cm^3\ molecule^{-1}\ s^{-1}$. The kinetic data are discussed in terms of OH and Cl reactivity trends and comparisons are made with the existing literature values and with rate coefficients from structure activity relationship methods. This is the first study on the rate coefficient determination of the reaction of ethylcyclohexane with OH radicals and chlorine atoms, respectively.

Introduction

Cycloalkanes are often used as radical scavengers in studies of atmospheric chemistry due to their relatively fast kinetics and mechanistically simple oxidation[1,2]. Recently, the University of Leeds, Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)[3] has been used to provide an alternative calibration method for OH detection via the FAGE (Fluorescence Assay by Gaseous Expansion) method[4,5] by monitoring decays of cyclohexane[6]. As a fluorescence technique, FAGE needs calibration and conventionally this is achieved by introducing known concentrations of OH generated from water photolysis at 185 nm, into the FAGE apparatus[7]. This calibration technique is limited to ambient pressures and temperatures, but when operating on an airborne platform, FAGE may be sampling air under conditions that are very different from those under which it was calibrated. Additionally, typical OH calibration concentrations are several orders of magnitude greater than day time ambient values of ~ 10^6 molecule cm^{-3}[8]. We have used the hydrocarbon decay method to provide an alternative calibration method [6]. For this technique, higher values of the rate coefficient for OH + hydrocarbon, k_{OH}, and a simple pressure independent mechanism, provide more accurate results.

Cyclohexane has been used in our previous OH calibration work[6], but the presence of tertiary C-H bonds in alkyl substituted cyclohexanes and hence the potential of higher k_{OH} values, makes these compounds more attractive and provides the main motivation for this study. Future work will extend our evaluation of calibration techniques to a wider range of temperature. The temperature dependence of cyclohexane with OH radicals has been extensively studied and is summarized in Calvert et al.[9]. However, alkyl substituted cycloalkanes have received much less attention, only the methylcyclohexane rate coefficient with OH has been studied as a function of temperature[10].

Additionally, cycloalkanes are one of the major classes of constituents of the trace-gas composition of the atmosphere making important contributions to atmospheric chemical systems with implications from local to global scale[9]. An important constituent of vehicle fuels, cycloalkanes have been found in the emissions from motor vehicles [11,12] and in road tunnels[13]. Cycloalkanes are widely used as solvents in the manufacture of rubber, machinery and plastics. Not surprisingly, given these sources, cycloalkanes have been detected in the urban atmosphere[14]. Cycloalkanes have been also detected in atmospheric emissions near the Deepwater Horizon oil spill event [15] and over oil sands mining operations[16]. Like other alkanes, cycloalkanes are potential sources of ozone[17].

Only abstraction reactions with the atmospheric oxidants OH radicals and Cl atoms contribute significantly to cycloalkane oxidation[9]. From the group of cycloalkanes, cyclohexane has the lowest strain energy. The strain energy influences the kinetics of cycloalkanes toward OH radicals[9]. Cycloalkanes with no strain energy (cyclohexanes) possess higher reactivity toward abstraction of hydrogen atoms than corresponding linear chain alkanes due to the presence of two more secondary hydrogen atoms than the linear alkanes, the chains of which are terminated with methyl groups containing less reactive primary hydrogen atoms. Alkyl substituted cycloalkanes have gained less attention than their non-substituted homologues.

Although OH is the primary radical initiator of hydrocarbon oxidation in the atmosphere, atomic chlorine can be an important initiator under certain circumstances and Cl atoms are often used as a convenient method of initiating oxidation in chamber studies[18]. Chlorine is present in the atmosphere in various forms from a range of processes [19-22]; although ambient Cl concentrations are much lower than OH, chlorine atoms can play an important role in atmospheric chemistry since their reactions with hydrocarbons are typically several orders of magnitude greater than the corresponding OH reaction. The concentration of Cl atoms in coastal areas could reach as much as 1×10^5 atom cm^{-3} for a brief period at dawn[23] and there is evidence for an influence of atomic chlorine, derived from $ClNO_2$, over continental landmasses[24].

At room temperature, Aschmann and Atkinson [25] have determined the rate coefficient of Cl with methylcyclohexane ($(3.47\pm0.12)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} using a relative method with n-butane as the reference compound in a reaction chamber with Cl atoms being produced by Cl_2 photolysis with black lamps. The rate coefficient for the reaction of methylcyclohexane with OH radicals has been reported at 1 atm and room temperature with very good agreement between the values measured by Atkinson et al.[26], $(10.6 \pm 0.3)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and Kramp and Paulson [27], $(9.4\pm0.6)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, determined using relative rate techniques, and with the room temperature determination of Sprengnether et al.[10], $(9.3 \pm 0.1)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} measured using a discharge flow, laser induced fluorescence technique. In 2015, Ballesteros et al.[28] reported the room temperature rate coefficients for a series of methylated cyclohexanes with OH radicals and chlorine atoms. The rate coefficients obtained by Ballesteros et al. were determined using a relative kinetic technique, with experiments being performed in a small (16L) borosilicate glass cylinder and the result for the reaction of OH with methylcyclohexane, $k_{OH+MCH}=(11.8\pm1.2)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, is slightly higher than the previous studies, but still in agreement, within the mutual error limits.

To our knowledge this work is the first rate coefficient determination for the reaction of OH radical and Cl atom with ethylcyclohexane, whereas for trans-1.4-dimethylcyclohexane only one study has been previously reported by Ballesteros et al.[28]. Additionally, this is only the second reported Arrhenius equation for the methylcyclohexane reaction with OH radicals over atmospherically relevant temperatures.

Experimental

The relative kinetic technique has been applied to investigate the kinetics of the reactions of OH radicals and chlorine atoms with methylcyclohexane (MCH), trans-1,4-dimethylcyclohexane (DCH) and ethylcyclohexane (ECH) at ~293 K and 760 Torr of synthetic air.

$Cl + CH_3\text{-c-}C_6H_{11} \rightarrow \text{products}$ R1

$Cl + CH_3\text{-c}C_6H_{10}\text{-}CH_3 \rightarrow \text{products}$ R2

$Cl + CH_3CH_2\text{-c-}C_6H_{11} \rightarrow \text{products}$ R3

$OH + CH_3\text{-c-}C_6H_{11} \rightarrow \text{products}$ R4

$OH + CH_3\text{-c}C_6H_{10}\text{-}CH_3 \rightarrow \text{products}$ R5

$OH + CH_3CH_2\text{-c-}C_6H_{11} \rightarrow \text{products}$ R6

Most kinetic measurements were performed in the HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) photoreactor, described in detail elsewhere.[3] HIRAC is a ~2 m^3 stainless steel cylindrical reactor. The photolysis processes for Cl_2 and methylnitrite were initiated by irradiation with eight blacklamps (Philips TL-D/36 W BLB; $320 \text{ nm} < \lambda < 420 \text{ nm}$, $\lambda_{max}=365$ nm) housed within eight evenly distributed, temperature controlled quartz tubes inside the reactor. Mercury lamps housed in the same quartz tubes were used to generate OH radicals from hydrogen peroxide photolysis predominantly at 254 nm.

The photolysis of $Cl_2$was used as the Cl atom source:

$Cl_2 + h\nu\ (320 \text{ nm} < \lambda < 420 \text{ nm}) \rightarrow 2Cl$ R7

The photolysis of methyl nitrite (CH_3ONO) in the presence of NO was used as the OH radical source for majority of the OH experiments with MCH (R4):

$CH_3ONO + h\nu\ (320\ \text{nm} < \lambda < 420\ \text{nm}) \rightarrow CH_3O + NO$ R8

$CH_3O + O_2 \rightarrow HCHO + HO_2$ R9

$HO_2 + NO \rightarrow OH + NO_2$ R10

Experiments on the kinetics of OH with DCH and ECH were initiated by the photolysis of H_2O_2 (R11):

$H_2O_2 + h\nu\ (\lambda\ \text{predominantly}\ 254\ \text{nm}) \rightarrow 2OH$ R11

Additionally, the ozonolysis of trans-2-butene (t2B, C_4H_8) was used as an OH radical source in the room temperature studies of R4.

$O_3 + C_4H_8 \rightarrow OH + \text{products}$ R12

O_3 was produced by photolysis of oxygen passed through an external cell irradiated with a pen-ray lamp at 185 nm. The ozone concentration was monitored using a UV photometric O_3 analyzer (model TEC 49C) with a detection limit of 1 ppbv for a 30 s measurement period. O_3 was mixed with the air, MCH and cyclohexane (CH, the reference) using fans located within HIRAC. The reaction was initiated by the injection of trans-2-butene. To our knowledge only one previous kinetic study with OH radicals involved the ozonolysis of alkenes as the OH radical source[29].

A Chernin-type multiple reflection mirror system[30] operated at a total optical path length of 128.52 m coupled to a Bruker IFS/66 FTIR spectrometer was used for reactant and reference compound detection. The IR spectra were recorded at a spectral resolution of 1 cm^{-1} in the range 700 – 4000 cm^{-1} using a KBr beamsplitter and external liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector. Typically, 100 interferograms were co-added per spectrum. Each spectrum requires around two minutes acquisition time. The data were collected over different time periods for each type of reaction, from 20 min for chlorine initiated reactions to 60 min for the OH radical initiated reaction when OH was produced by the ozonolysis of trans-2-butene.

Additional to the FTIR measurements, gas chromatography with flame ionization detection (GC-FID, Agilent 6890N) was used for online detection of the compounds. Gas samples were injected onto the column (Varian Chrompack CP-Sil 5CB column, 50 m, 0.32 mm i.d. and film thickness of 5 μm) every 2 min, with helium as the carrier gas. The separation method (flows and oven temperatures) varied dependant on the mixture of the compounds to be separated. The online sampling system was based on the collection of chamber samples into

5 ml evacuated sampling loops. Samples are injected afterwards, through a 2-position 6-way multiport valve controlled by the GC. Between the injections the sampling line was evacuated.

Prior to the reaction with OH radicals or Cl atoms the wall loss deposition, dilution and possible artefacts or interferences were monitored in the dark over a period of 10 min (5 GC samples and/or 5 FTIR spectra). No wall loss was observed for the alkylated cyclohexanes and reference compounds employed in this study. The dilution due to the sampling on the GC-FID is minimal. Also no cycloalkane decay was observed due to interfering processes, for example removal by Cl_2 when investigating the reactions of alkyl cyclohexanes with Cl atoms, or reaction with O_3 for those studies where OH was generated by ozonolysis.

The OH radicals/Cl atoms will react with both the alkyl cyclohexane, ACH, and the reference hydrocarbon:

$$\text{ACH} + \text{OH/Cl} \longrightarrow \text{products} \qquad (k_{ACH}) \tag{1}$$

$$\text{Reference} + \text{OH/Cl} \longrightarrow \text{products} \qquad (k_{REF}) \tag{2}$$

For the systems under investigation the following kinetic expression applies:

$$\ln\left(\frac{[\text{ACH}]_0}{[\text{ACH}]t}\right) = \frac{k_{ACH}}{k_{REF}} \ln\left(\frac{[\text{reference }]_0}{[\text{reference }]t}\right) \tag{3}$$

where $[\text{ACH}]_0$, and $[\text{reference}]_0$ are the concentrations of the ACH and reference compounds at time t = 0, respectively, and $[\text{ACH}]_t$, and $[\text{reference}]_t$ are the concentrations at time t. Plots of $\ln([\text{ACH}]_o/[\text{ACH}]_t)$ vs $\ln([\text{reference}]_o/[\text{reference}]_t)$ should yield a straight line with slope k_{ACH}/k_{REF} and zero intercept.

Two reference compounds have been used for the determination of the rate coefficients of the reaction of Cl atoms with alkylcylohexanes:trans-2-butene (t-2B) and cyclohexane (CH). The rate coefficients for the reference reactions with Cl atoms are $k_{(Cl + t\text{-}2B)} = (3.50 \pm 0.50)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}[31]and $k_{(Cl + CH)} = (3.30\pm0.49)\times10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}[9]. For t-2B, the value determined by Kaiser et al. [31] was chosen as the most comprehensive recent study and for cyclohexane, the rate coefficient is from a recent critical review by Calvert et al. [9].

Additionally, in preparation for temperature dependent FAGE calibration studies, the reaction of MCH with OH radicals has been studied over the temperature range 273 to 343 K using only the photolysis of CH_3ONO as a source of OH radical while the room temperature rate coefficients have used ozonolysis with CH as a reference and H_2O_2 photolysis with CH and isopentane as reference compounds. For the reaction of DMCH and ECH with OH radicals, H_2O_2 photolysis has been used as the primary source of OH radicals with CH, isopentane and diethyl ether as reference compounds. Reference hydrocarbons (and their recommended rate coefficients in cm^3 $molecule^{-1}$ s^{-1}) used in the OH study were: cyclohexane (CH); $k_{(OH + CH)}$ = $(3.26\times10^{-17})\times T^2 \exp[(262)/T]$ [32], toluene; $k_{(OH + C7H8)}= (5.7 \pm 1.5) \times 10^{-12}$ [33], isopentane; $k_{(OH + iC5H12)}= (3.6 \pm 1.1) \times 10^{-12}$ diethyl ether; $k_{(OH + C4H10O)}= (1.32 \pm 0.13) \times 10^{-11}$ [34], ethene; $k_{(OH + C2H4)}= (8.7 \pm 2.2) \times 10^{-12}$ [35], propene; $k_{(OH + C3H6)}= (2.63 \pm 0.66) \times 10^{-11}$ [35].

Compounds (MCH, DMCH, ECH, CH, CH_3ONO, NO, toluene, t-2B, Cl_2) were added into the reactor from a known partial pressure in a 1 litre vessel using a flow of nitrogen. The initial concentrations (in units of molecule cm^{-3}) were: ACH, 4-6×10^{13}; CH_3ONO, ~ 8×10^{13}; NO, ~ 3×10^{13}; toluene, 4-6 × 10^{13}; trans-2-butene, 2-4×10^{13} when used as reference in ACH + Cl reactions and ~ 8×10^{13} when used as precursor of OH radicals in the ozonolysis experiments. Various concentrations of O_3 up to 12.5 × 10^{13} molecule cm^{-3} have been used in the OH radical initiated rate coefficient determinations. Cl_2 concentrations did not exceed 15 ×10^{13} molecule cm^{-3}.

In addition to the experiments performed in HIRAC chamber, a few experiments on the kinetics of ECH with OH radicals have been performed in QUAREC (QUArtz REaction Chamber) in Wuppertal, Germany to check for any systematic differences. The QUAREC chamber is described in detail elsewhere[36,37]. Briefly, the chamber consists of a cylindrical quartz cylinder, volume 1080 l, evacuated between the experiments to 10^{-2} mbar with a turbomolecular pump. At the both ends the chamber is equipped with a number of sampling and injection ports. Mixing inside the chamber is managed by 3 fans. The reactor is surrounded by 32 photolysis lamps which emit light in the range of $300 \text{ nm} < \lambda < 460 \text{ nm}$, $\lambda_{max} = 360$ nm). Monitoring of the reactant and reference compounds was performed using a FTIR instrument, Thermo Nicolet, coupled to a White-type multiple reflection mirror system mounted inside the chamber with a total optical path length of 484±0.8 m. The FTIR spectrometer has a liquid nitrogen cooled mercury−cadmium−telluride (MCT) detector. IR spectra were recorded at a resolution of 1 cm^{-1} in the range 700−4000 cm^{-1}. Typically, 120 co-added interferograms per spectrum were collected leading to a time resolution of around 1 min.

All the alkylated cyclohexanes used in this study were obtained from Aldrich and used without further purification. Their purities were as follows: MCH, >99%; DCH, >98% and ECH, >99%. The reference compounds used in this study had the following specifications:

trans-2-butene, 99+% (Aldrich), toluene and cyclohexane 99% (Fisher Scientific).Cl_2 (Aldrich) had a purity of > 99.5%. The method of Taylor et al.[38] has been used for the synthesis of methylnitrite. Ultra-high-purity (UHP) 1:4 synthetic air was obtained by a mix of O_2 (BOC, zero-grade, >99.999 %) and N_2 (BOC, zero-grade, >99.998 %).Experiments in QUAREC chamber have been performed using synthetic air provided by Air Liquide with a purity >99.999 %.

Initial experiments with reaction R5, OH + DCH with toluene as the reference compound and with OH being generated from H_2O_2 photolysis, produced surprising results, the origin of which was traced to toluene photolysis from a small amount of 185 nm light from the mercury lamps and sensitisation reactions. In attempting to identify the issues, we also carried out some laser flash photolysis studies of reaction R5. Details of the apparatus used can be found in previous publications [39-41]. Briefly, OH radicals were generated by the pulsed laser photolysis of H_2O_2 at 248 nm in a slow-flow cell and reacted with excess DCH in a bath gas of nitrogen (total pressure 200 Torr). The exponential decay of OH radicals was monitored by pulsed laser induced fluorescence tuned to ~282 nm to match a rovibrational channel in the A – X transition of OH. The resulting fluorescence at ~308 nm was passed through a filter ((308 ± 5) nm) and collected on a channel photomultiplier tube (Perkin-Elmer C1943P), mounted perpendicularly to the gas stream and probe radiation beam. The delay between the photolysis and probe pulses was systematically varied by a delay generator (BNC 555) to build up an OH time profile (see inset to figure in the results section for a typical example) including information on the pre-photolysis background level of OH. Each trace typically consisted of 200 points (with 20 points providing pre-trigger background) and the final trace was typically an average of 5 – 10 repetitions.

OH reacted under pseudo-first-order conditions; in this regime, the concentration of OH as a function of time is given by:

$$[OH]_t = [OH]_0 e^{-k't} \tag{4}$$

where k’ is the pseudo-first-order rate coefficient given by:

$$k' = k_5[DCH] + k_{1st} \tag{5}$$

Here k_5 is the bimolecular rate coefficient for reaction R5 and k_{1st} represents the rate coefficient for the loss processes due to diffusion and reaction of OH with the constant concentration of precursor. Under these conditions, a plot of k’ vs [DCH] should give a straight line where the gradient is k_5 and the intercept is the sum of the first order loss processes. An example of such a bimolecular plot is shown in the results section.

Results

(i) Reaction with chlorine atoms

An example of the relative rate data obtained for the reaction of chlorine atoms with DCH (R2) are plotted according to Equation 3 in Figure 1; Figures S1 and S2 in the Supplementary Information show equivalent plots for reactions R1 and R3. At least two experiments were recorded for each reference compound involved in this study. All the plots show very good linearity for both reference hydrocarbons used in this study, cyclohexane and trans-2-butene. Table 1 lists the rate coefficient ratios k_{ACH}/k_{REF} determined from the plots and the absolute values of the rate coefficients, k_{ACH}, calculated for the reactions of Cl with the three alkylcyclohexane compounds investigated. The errors quoted in Table 1 for the rate coefficients k_{ACH} include the 2σ statistical error obtained from the linear regression analyses of the plots, plus a 20% contribution from the uncertainty in the recommended values of the rate coefficients for the reference compounds. The quoted errors for the rate coefficients ratios k_{ACH}/k_{REF} are only the 2σ statistical errors.

(ii) Reaction with OH radicals

Temperature dependent rate coefficients for the reaction of methylcyclohexane with OH radicals have been obtained over the temperature range 273 K to 343 K using cyclohexane as the reference hydrocarbon. Room temperature rate coefficients for three ACH with OH radicals have been determined at ~293 K in the HIRAC chamber using a relative kinetic method and FTIR and GC-FID as detection techniques. Table 2 presents the rate coefficient ratios k_{ACH}/k_{REF} obtained from the plots and the absolute values of the rate coefficients, k_{ACH}, calculated for the reactions of OH radicals with MCH, DCH and ECH investigated in this study. The errors quoted have been calculated in the same way as for Table 1.

Figure 2 presents the kinetic data plotted for the MCH reaction with OH radical at different temperatures and the resulting Arrhenius plot is shown in Figure 3. The best fit line through the data gives:

$$k_{(OH + MCH)} = (1.71\pm 0.22)\times10^{-11} \exp((-1.62\pm 0.16)\text{kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors are only statistical at the 2σ level. The rate coefficients of methylcyclohexane with OH radicals in the temperature range of 273 – 343 K exhibit a slight positive temperature dependence, consistent with a simple abstraction mechanism. Errors included for room temperature rate coefficients are the average of the assumed 20% error for the reference rate coefficient and the 2σ error from the slope. Figures 4 and 5 and the data in Table 2 show very good agreement for the rate coefficients for reaction R4 when two different OH radical generation processes (CH_3ONO photolysis or ozonolysis) have been used.

In addition to MCH rate coefficient determination for the reaction with OH radicals, two other alkylated cyclohexanes have been investigated, DCH and ECH with OH being produced by H_2O_2 photolysis. Both GC-FID and FTIR analysis have been used for monitoring the decay of reactant and reference compounds. Reaction R5 was also studied using direct laser flash photolysis methods as described above. An example of a bimolecular plot from which k_5 can be extracted is shown in Figure 6; the inset shows a typical OH exponential decay.

Discussion and conclusions

Cyclohexane reactions have not received as much attention as open chain alkanes so an evaluation by comparison with other rate coefficients is limited. Previous literature data, where available, have been included in Tables 1 and 2. Using structure-activity relationship (SAR) methods it is possible to obtain the rate coefficient values to compare with the values obtained in this study. The SAR method is based on the partial contribution of each reactive site to the overall rate coefficient value. These approaches are used by the US Environmental Protection Agency in the AOP WIN estimation programme (U.S.EPA, 2011).

The SAR estimations of the rate coefficients of Cl radical initiated reaction with alkylcyclohexanes are presented in Table 1 where they are compared with the values determined in this study. For the reaction of Cl atoms with MCH (R1), there is good agreement with the literature values [25,28] and with the SAR of Tyndall et al.[42]. The SAR of Aschmann and Atkinson [25] predicts a slightly lower value, but still within the error bars of the current determinations. This work, Ballesteros et al. [28] and the SAR are consistent in determining or predicting that the rate coefficient for Cl with DCH (R2) is essentially identical, within error, to that of reaction (R1). For the rate coefficient of the reaction Cl + ECH (R3), a more significant increase is observed over the rate coefficient for Cl + MCH (11%), again qualitatively consistent with the predictions of the SAR. In general the agreement between experiment and SAR is very good as has been noted in previous studies on Cl + alkane kinetics [43,44]. However, the absolute values for the rate coefficient for Cl + DCH from this work and Ballesteros et al. do not overlap and the Ballesteros value is approximately 20% lower than that determined in this study. Cyclohexane was used in both relative rate studies for and so here the relative rates (the primary experimental data) can be compared. Ballesteros et al. report a value of k_{Cl+DCH}/k_{Cl+CH} 14% lower than this work. There is no obvious reason why there should be such a discrepancy in the primary experimental data. Both relative rate studies use a range of detection methods (FTIR and chromatography) which should highlight any systematic errors such as co-elution with product peaks. The slightly higher values for the rate coefficients of Cl + DCH is also mirrored in the MCH work (however, here the error bars do overlap). For Cl + MCH, our higher value is in excellent agreement with the study of Aschmann and Atkinson [25].

As can be seen from Table 2 and Figures 4 and 5, the various methods of OH generation (methylnitrite or H_2O_2 photolysis and ozonolysis of t-2B) give good agreement, independent of the method of analysis (GC-FID or FTIR) or reference compound (cyclohexane or toluene) for the reaction of OH with MCH (R4). Figure 5 demonstrates that the signal to noise for O_3 initiated reactions is not as good as for photolytic initiation. It is possible that conditions could be further optimized, however, this study does demonstrate the potential for studying OH reactions with photo-labile species. There is also excellent agreement between the rate coefficients determined for reaction (R6), OH + ECH, determined in HIRAC and QUAREC. An example of data from QUAREC can be found in Supplementary Information (Fig S3).

There have been very limited previous kinetic studies using ozonolysis of alkenes as the OH source [29]; potentially the method has two important advantages in being non-photolytic and not requiring the addition of NOx to the reactor. The avoidance of NOx can be important in some chambers, e.g. EUPHORE or SAPHIR, where it is difficult to evacuate the chamber and residual NOx may interfere with subsequent studies. The presence of NOx can also cause interferences in the FAGE detection method [45]; having a range of validated OH sources for calibration/interference studies is relevant to our future work. Of course ozonolysis has its own disadvantages; a range of co-products are formed which could influence studies, the rate coefficients under study need to be reasonably fast otherwise a majority of OH loss occurs via reaction with the alkene (t-2B in this study) resulting in limited consumption of the alkanes under investigation and of course there must be no reaction of the substrate or reference with ozone. The scatter in the relative rate plots for the ozonolysis initiated reactions was significantly greater than other plots and we have therefore given significantly less weight to these data in our evaluation of the average room temperature rate coefficient presented in Table 2.

The methylcyclohexane room temperature rate coefficient for the reaction with OH radicals has been studied by Atkinson et al.[26], Kramp and Paulson [27] and more recently by Sprengnether et al.[10] and Ballesteros et al.[28] The room temperature rate coefficient, $k_{4,293\ K}$, for reaction of OH with MCH determined in this study, (9.5 ± 1.3)× 10^{-12} cm^3 $molecule^{-1}$ s^{-1} is at the lower end of the reported determinations, in good agreement with the direct studies of Sprengnether et al. and the relative rate studies of Kramp and Paulson. The value from Atkinson et al.[26]((10.6 ± 0.3) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) is slightly higher than this work and recent literature, however, using the most recent IUPAC recommendation for the rate coefficient for OH + n-butane reference reaction, brings the rate coefficient into excellent agreement with this work ((9.7 ± 0.3) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}). The most recent determination is a relative rate study by Ballesteros et al., reporting a value ~22% higher than this work, but still within the combined error ranges.

Sprengnether et al.[10] have investigated k_4 over the temperature range 230-379 K at 8-10 Torr pressure of nitrogen. The results of this study and our work is presented in Figure 3 and there is good agreement (better than 15%) in the absolute rate coefficients over the common temperature range although our data are systematically slightly lower in magnitude. Our measured activation energy ((1.62 ± 0.16) kJ mol^{-1}) is slightly greater than that obtained from a linear Arrhenius fit to the Sprengnether et al. data ((1.24 ± 0.30) kJ mol^{-1}) although the error bars do overlap. The temperature dependence of our study depends on both the temperature dependence of the relative rate and the reference reaction (OH + CH). We have used the temperature dependence recommended by Atkinson et al. [32] and the temperature dependence is in good agreement (10 – 20%) with other studies including Sprengnether et al. and Droege and Tully [46]. Sprengnether et al. measured the temperature dependence of three other non-branched alkylcycloalkanes and the activation energies for these reactions were approximately 50% greater than for MCH. Our study confirms the weak positive temperature dependence for the OH + MCH, but suggests that the temperature dependence is slightly stronger than that reported by Sprengnether et al. The spread in the value of the room temperature rate coefficients for OH + MCH from this study suggests that the errors in the A factor are greater than the statistical error from the Arrhenius fit. Our recommended Arrhenius expression incorporates the activation energy from our relative rate study with cyclohexane as the reference, but with the A factor scaled to agree with our average room temperature rate coefficient of (9.5 ± 1.3) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The resulting expression is:

$$k_{(MCH + OH)} = (1.85 \pm 0.27)\times10^{-11} \exp((-1.62 \pm 0.16)\ kJ\ mol^{-1}/RT)\ cm^3\ molecule^{-1}\ s^{-1}$$

Apart from one study on the kinetics of DCH [28] with OH radicals at 298 K, no other literature data are available for DCH and ECH. For DCH, there is good agreement between the relative rate studies and the direct measurement using laser flash photolysis/laser induced fluorescence. Given that these are very different approaches to determining rate coefficients, it would suggest that our results are free from significant systematic errors. Our initial relative rate studies using H_2O_2 photolysis at 254 nm and toluene as a reference compound demonstrate that a significant interference occurs with aromatic reference compounds and these should be avoided.

The substitution of H atoms by the alkyl groups ($-CH_3$, $-C_2H_5$) in cycloalkane increases the rate coefficients over those for OH + CH due to the faster H atom abstraction from tertiary C-H compared to the secondary C-H bond in cyclohexane. As would be expected due to presence of secondary C-H bonds in the alkyl side chain, ECH reacts faster with OH than MCH, in good agreement with SAR predictions. OH reacts faster with DCH than MCH due to the presence of a second tertiary C-H bond. Whilst both DCH and ECH react slightly faster than MCH, their lower vapour pressures make them more difficult to work with and therefore CH and MCH are probably the most practical species for further in situ OH calibration studies in HIRAC.

Using the kinetic data obtained in the present study in combination with a daytime average radical concentrations allows for the estimation of the tropospheric lifetimes, $\tau_{OH/Cl}$, using:

$$\tau_{OH/Cl} = 1/k_{(OH/Cl + ACH)}[OH/Cl]$$

Accordingly, for a globally averaged [OH] of 1×10^6 cm^{-3}[8], the atmospheric residence times for the MCH, DCH and ECH are estimated to be around 20-30 hours (see Table 2). Cl atom concentrations are more spatially variable. In highly polluted regions or coastal locations [Cl] can range from $1 - 5 \times 10^4$ atom cm^{-3} [23,46]. With [Cl] at the upper end of this range, atmospheric lifetimes for MCH, DCH and ECH are between 13 – 16 hours (see Table 1) and Cl chemistry can contribute significantly to their removal. However, global levels are significantly lower, typically ~500 atom cm^{-3} [46]; in these regimes, removal will be dominated by reaction with OH. With lifetimes of approximately one day, alkyl cyclohexanes will contribute only to local air pollution.

Acknowledgements

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Figure captions:

Figure 1. Plot of the kinetic data according to eq (3) for the reaction of Cl atoms with methyl cyclohexane (MCH) using (●,▼) trans-2-butene and (■,▲) cyclohexane as the reference hydrocarbon. The data have been displaced vertically for clarity.

Figure 2. Plot of the kinetic data according to eq (3) for the reaction of OH radicals (CH_3ONO photolysis) with MCH using cyclohexane as the reference hydrocarbon at five different temperatures. The data have been displaced vertically for clarity.

Figure 3. Arrhenius plot of the rate constants for the reaction of OH radicals with MCH (■) this work, (●) Sprengnether et al. (2009). The linear fits to the data are: this work, k_4 =(1.71 ± 0.22)$\times 10^{-11}$exp(-(1.62 ± 0.16) kJ mol^{-1})/RT) cm^3 molecule^{-1} s^{-1}, Sprengnether et al., k_4 =(1.59 ± 0.20)$\times 10^{-11}$exp(-(1.24 ± 0.30) kJ mol^{-1})/RT) cm^3 molecule^{-1} s^{-1}. The errors represent statistical errors at the 2σ level.

Figure 4. Kinetic data plotted according to eq (3) for the reactions of OH radicals with MCH using cyclohexane as reference hydrocarbons and two different sources of OH radicals: trans-2-butene ozonolysis (●) and CH_3ONO photolysis (■).

Figure 5. Plot of the kinetic data according to eq (3) for the reaction of OH radicals (generated by the t2B+O_3 reaction) with methylcyclohexane (MCH) using (●,slope = 1.21 ± 0.11) and CH_3ONO photolysis (■, slope = 1.29 ± 0.02).

Figure 6. Main figure: Bimolecular plot of pseudo-first-order rate coefficient vs [DCH]. The gradient, (1.212 ± 0.015) × 10^{-11} cm^3 molecule^{-1} s^{-1}, is k_5. The error is the standard error at the 2σ level. Inset: Example of typical OH LIF temporal profile with exponential decay fit.

Table 1. Rate coefficients for the reactions of Cl atoms with methyl cyclohexane, 1,4 dimethyl cyclohexane and ethyl cyclohexane at 293 K.

Compound	Reference	k_{Cl+ACH}/k_{REF}	$10^{10}k_{ACH}$/cm^3 molecule^{-1} s^{-1}	10^{10} $k_{average}$/cm^3 molecule^{-1} s^{-1}	Lifetime	$10^{10}k_{SAR}$/ cm^3 molecule^{-1} s^{-1}	Literature values (10^{10}k/ cm^3 molecule^{-1} s^{-1})
Methyl cyclohexane (MCH)	Cyclohexane[a]	1.04±0.01	3.42±0.52	3.51±0.37	66 days[c]	3.58[42] 3.24[25]	3.47 ± 0.11[25][e] 3.11 ± 0.16[28]
	trans-2-butene[b]	1.03±0.02	3.60±0.52		16 hrs[d]		
trans-1,4-dimethyl cyclohexane (DCH)	Cyclohexane	1.06±0.04	3.51±0.54	3.63±0.38	64 days[c]	3.64[42] 3.37[25]	2.89 ± 0.16[28]
	trans-2-butene	1.07±0.04	3.75±0.55		15 hrs[d]		
Ethyl cyclohexane (ECH)	Cyclohexane	1.16±0.03	3.81±0.58	3.88±0.41	60 days[c]	4.22[42] 3.82[25]	None
	trans-2-butene	1.13±0.01	3.94±0.56		14 hrs[d]		

a Rate coefficient used (3.3 ± 0.49) × 10^{-10} cm^3 molecule^{-1} s^{-1} [9]

b Rate coefficient used (3.50 ± 0.50) × 10^{-10} cm^3 molecule^{-1} s^{-1} [31]

c [Cl] =500 atom cm^{-3} typical of global background [46]

d [Cl] =50000 atom cm^{-3} typical of polluted northern hemisphere or coastal location [46]

e n-butane as reference compound.

Table 2. Rate coefficients for the reactions of OH radicals with three alkyl cyclohexane (ACH) compounds at 293 K and methylcyclohexane in the temperature range 273 to 343 K.

Compound	Location, OH source and technique	Reference	k_{OH+ACH}/k_{REF}	$10^{12}k_{ACH}$/ cm^3 $molecule^{-1}$ s^{-1}	$10^{12}k_{av}$/cm^3 $molecule^{-1}$ s^{-1} (Lifetime, τ)[a]	$10^{12}k_{SAR}$/cm^3 $molecule^{-1}$ s^{-1}	Literature values ($10^{12}k$/cm^3 $molecule^{-1}$ s^{-1})
Methyl cyclohexane (293 K)	LEEDS, CH_3ONO, GC	Cyclohexane[b]	1.29 ± 0.01	8.8 ± 1.8	9.5 ± 1.3 (τ = 29 hrs)	9.28[26] 9.79[9]	10.6 ± 0.3 (9.7 ± 0.3)[c] [26] 9.4 ± 0.6 [27] 9.29 ± 0.13 [10] 11.8 ± 1.2 [28]
Methyl cyclohexane (293 K)	LEEDS, H_2O_2, GC	Cyclohexane[b]	1.37± 0.02	9.6 ± 1.9			
		Isopentane[d]	3.01± 0.26	10.9± 1.0 (3.3)[c]			
Methyl cyclohexane (293 K)	LEEDS, O_3+t-2B, GC and FTIR	Cyclohexane[b]	1.21 ± 0.22	8.3 ± 2.2			
		Toluene[e]	1.54 ± 0.28	8.8 ± 2.7			
Methyl cyclohexane Temperature dependent study	LEEDS, CH_3ONO, GC	Cyclohexane[b] 0°C	1.32 ± 0.01	8.38 ± 0.11[f]	$k_{(MCH + OH)} = (1.71\pm 0.22)\times10^{-11} \exp((-1.62\pm 0.16)\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$		
		Cyclohexane 35°C	1.25 ± 0.01	9.05 ± 0.14			
		Cyclohexane 50°C	1.22 ± 0.01	9.34 ± 0.11			
		Cyclohexane 70°C	1.18 ± 0.01	9.72 ± 0.09			
Trans-1,4-dimethyl cyclohexane	LEEDS, H_2O_2, GC	Diethylether[g]	0.77± 0.07	10.2± 1.4	12.1 ± 2.2 (τ = 23 hrs)	10.9[26] 11.0[9]	14.1 ± 1.5[28]
	LEEDS, H_2O_2, GC	Cyclohexane[b]	2.05 ± 0.05	14.3 ± 2.9			
	LEEDS, LIF, absolute technique			11.9± 1.2			

Ethyl Cyclohexane	LEEDS, H_2O_2, GC	Isopentane[d]	3.07± 0.19	11.0 ± 0.8 (3.3)[h]	11.8± 2.0 (τ = 24 hrs)	10.9[26] 11.7[9]	
Ethyl Cyclohexane	WUPPERTAL, CH_3ONO, FTIR	Ethene[i]	1.34 ± 0.07	11.6 ± 3.0			
		Propene[j]	0.49 ± 0.02	12.9 ± 3.3			

a The lifetime is calculated with $[OH] = 1 \times 10^{6}$ molecule cm^{-3} [8]

b The recommendation of Atkinson[32] is $k(T) = 3.26 \times 10^{-17} T^{2} \exp(262/T)$ cm^{3} $molecule^{-1}$ s^{-1} based on an evaluation of both absolute and relative rate experiments. The recommended uncertainty at room temperature is ± 20%

cThe value in brackets is using the latest IUPAC recommendation for the rate coefficient of the OH + n-butane reference reaction

d The error given is for the precision of the relative rate gradient (9%) and precision of the reference determination ($(3.60 \pm 0.10) \times 10^{-12}$ cm^{3} $molecule^{-1}$ s^{-1}), 3%). In his review of OH + alkane chemistry, Atkinson [32] recommends a conservative estimate of 30% in the uncertainty of the reference reaction and this is reflected in the error given in brackets.

e Reference value is $(5.7 \pm 1.5) \times 10^{-12}$ cm^{3} $molecule^{-1}$ s^{-1}[33]

f Errors in temperature dependent study are precision only.

g Estimated error of 10% in the reference reaction (1.32×10^{-12} cm^{3} $molecule^{-1}$ s^{-1}) which was obtained using direct methods (laser flash photolysis) [34].

h The error given is for the precision of the relative rate gradient (6%) and precision of the reference determination ($(3.60 \pm 0.10) \times 10^{-12}$ cm^{3} $molecule^{-1}$ s^{-1}), 3%). In his review of OH + alkane chemistry, Atkinson [32] recommends a conservative estimate of 30% in the uncertainty of the reference reaction and this is reflected in the error given in brackets.

iReference value is $(8.7 \pm 2.1) \times 10^{-12}$ cm^{3} $molecule^{-1}$ s^{-1} [35].

j Reference value is $(26.3 \pm 6.6) \times 10^{-12}$ cm^{3} $molecule^{-1}$ s^{-1} [35].

FIGURES

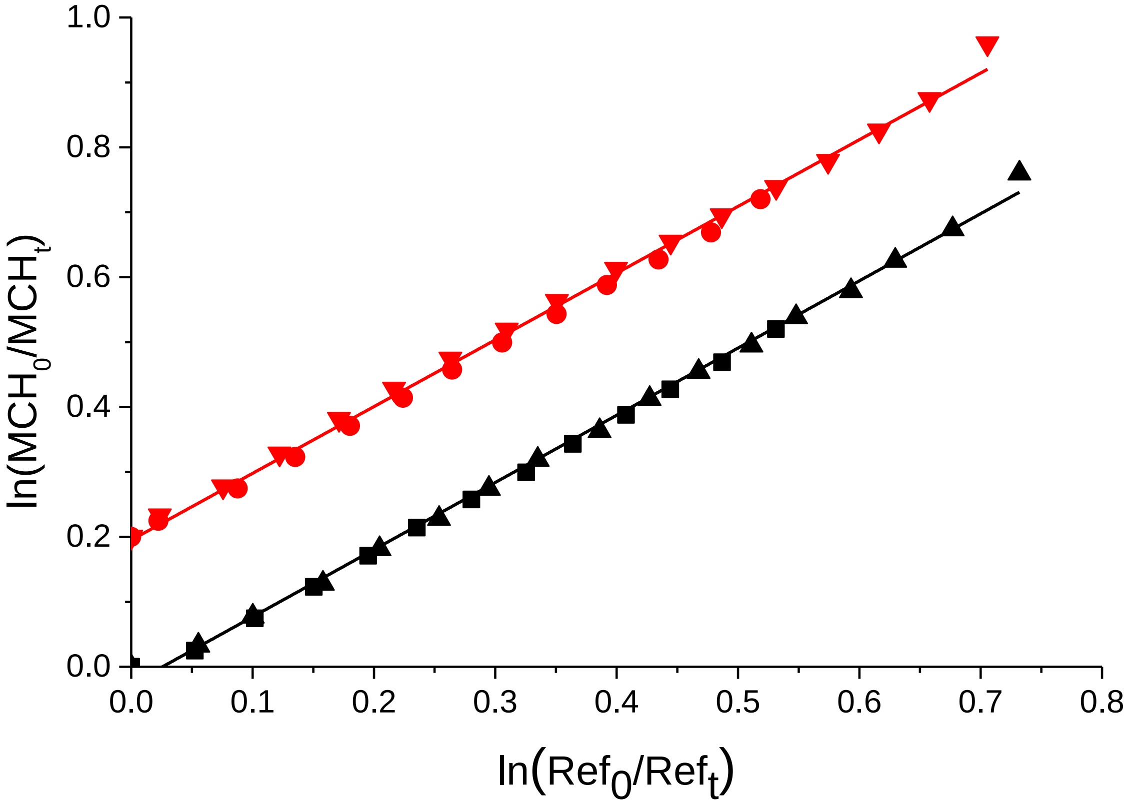


Figure 1. Plot of the kinetic data according to eq (3) for the reaction of Cl atoms with methyl cyclohexane (MCH) using (●, ▼) trans-2-butene and (■, ▲) cyclohexane as the reference hydrocarbon. The data have been displaced vertically for clarity.

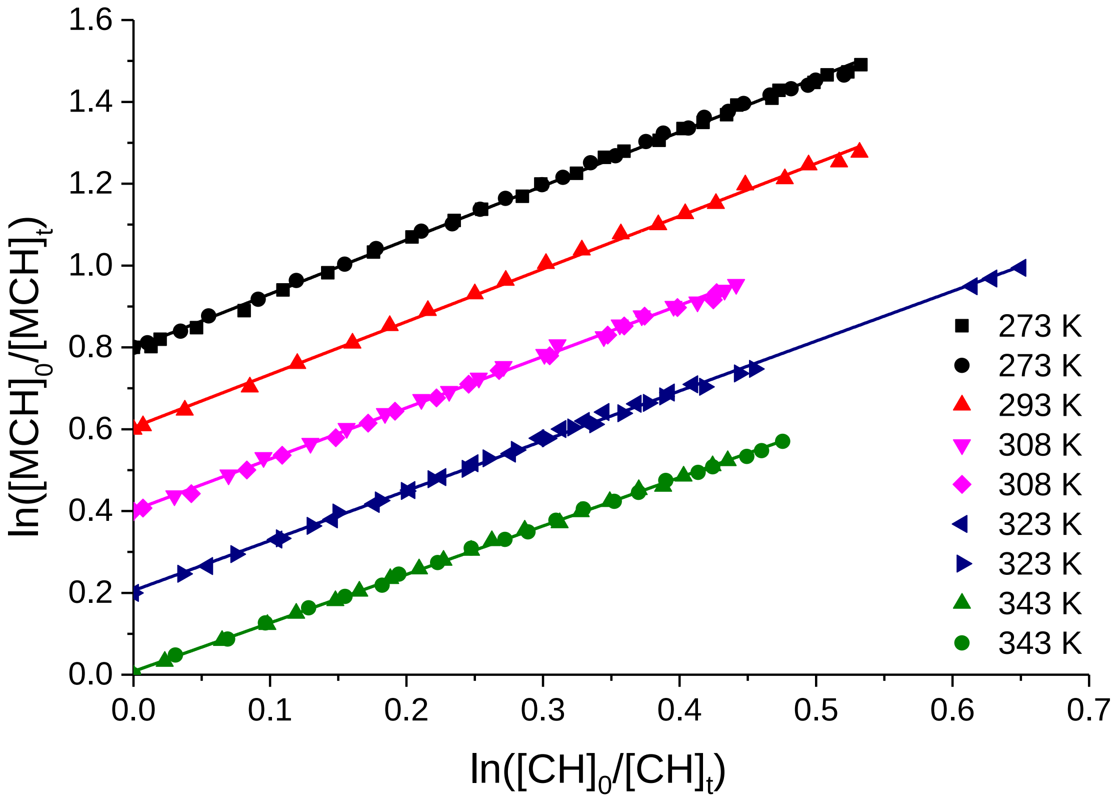
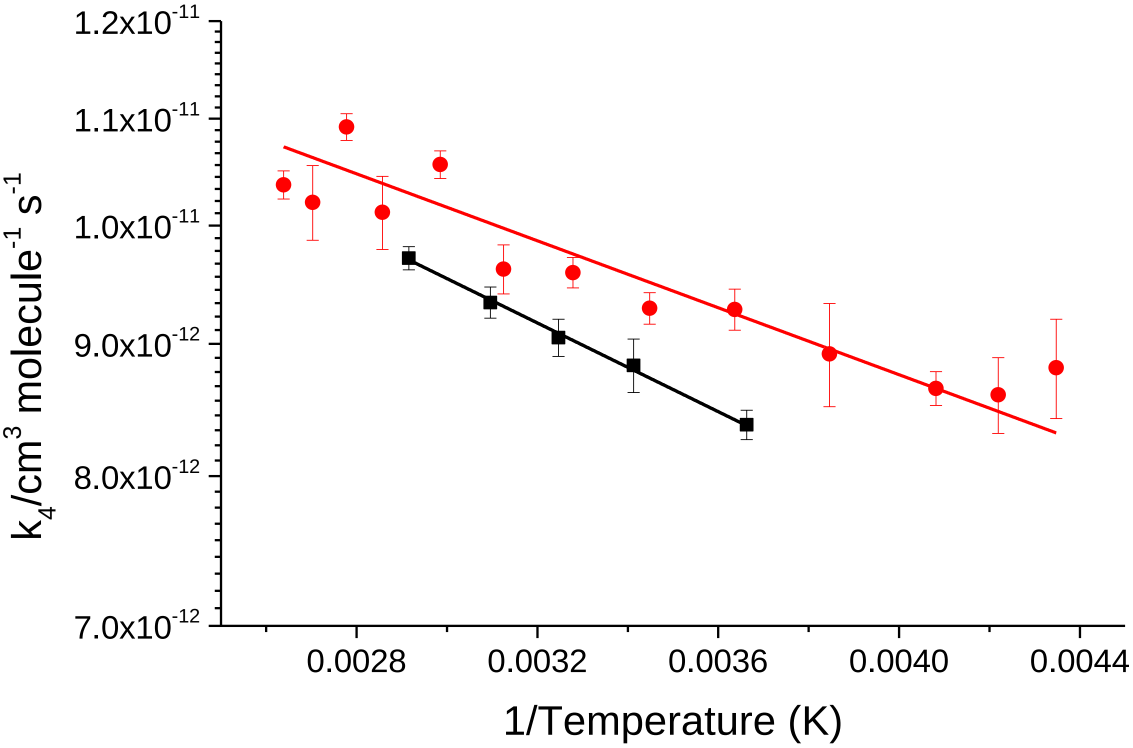


Figure 2. Plot of the kinetic data according to eq (3) for the reaction of OH radicals (generated from CH_3ONO photolysis) with MCH using cyclohexane as the reference hydrocarbon at five different temperatures. The data have been displaced vertically for clarity.



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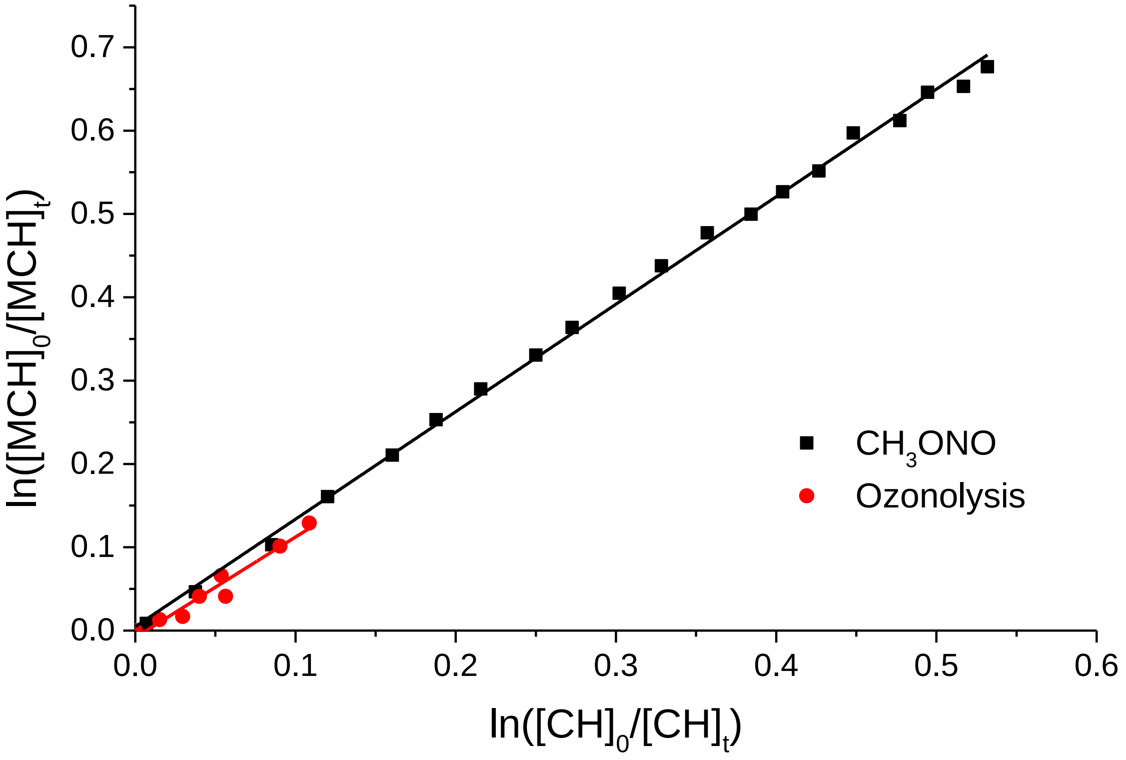

Figure 4. Kinetic data plotted according to eq (3) for the reactions of OH radicals with MCH using cyclohexane as reference hydrocarbons and two different sources of OH radicals: trans-2-butene ozonolysis (●, slope = 1.21 ± 0.11) and CH_3ONO photolysis (■, slope = 1.29 ± 0.02).

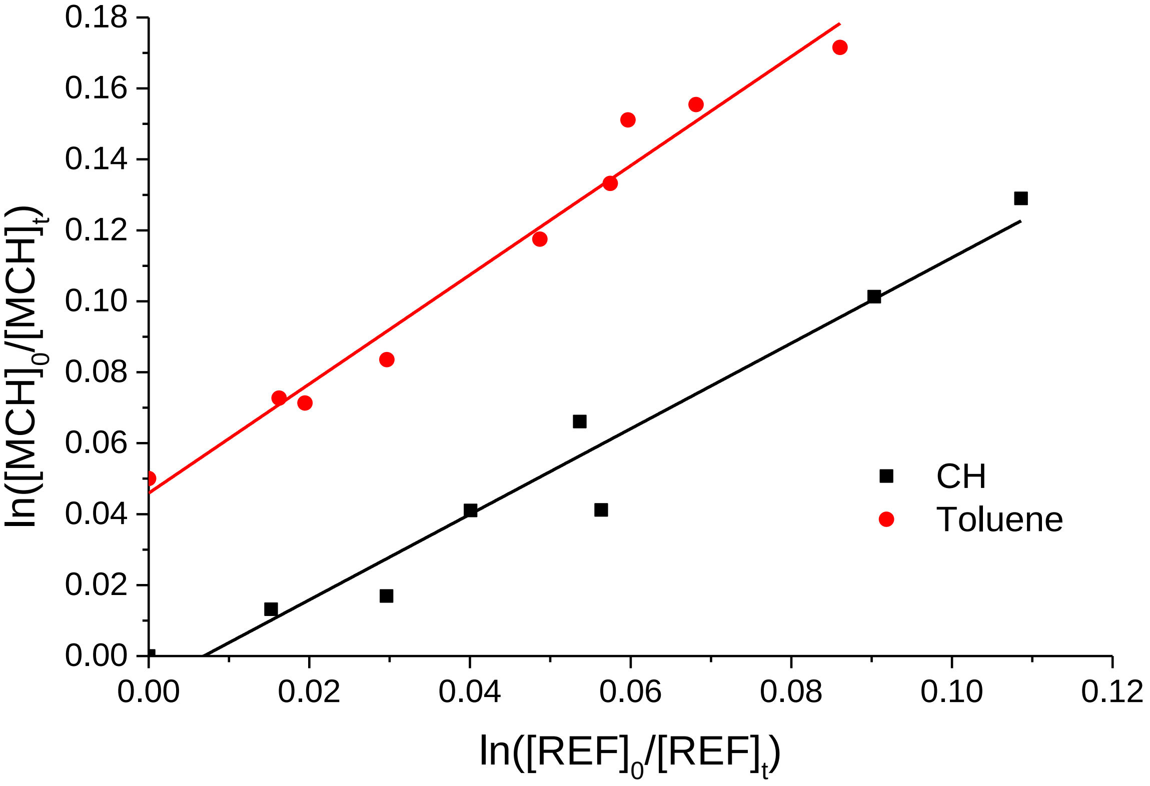

Figure 5. Plot of the kinetic data according to eq (3) for the reaction of OH radicals (generated by the t2B+O_3 reaction) with methylcyclohexane (MCH) using (●) toluene and (■) cyclohexane as the reference hydrocarbon.

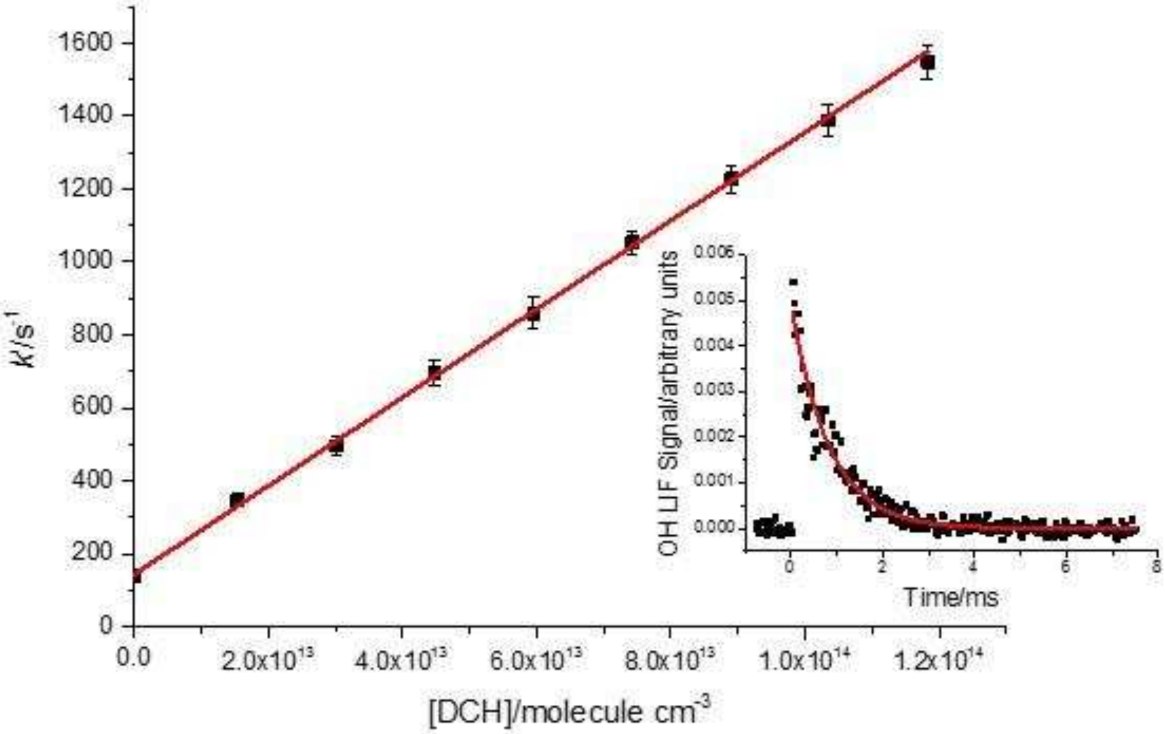

Figure 6. Main figure: Bimolecular plot of pseudo-first-order rate coefficient vs [DCH]. The gradient, (1.212 ± 0.015) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, is k_5. The error is the standard error at the 2σ level. Inset: Example of typical OH LIF temporal profile with exponential decay fit.

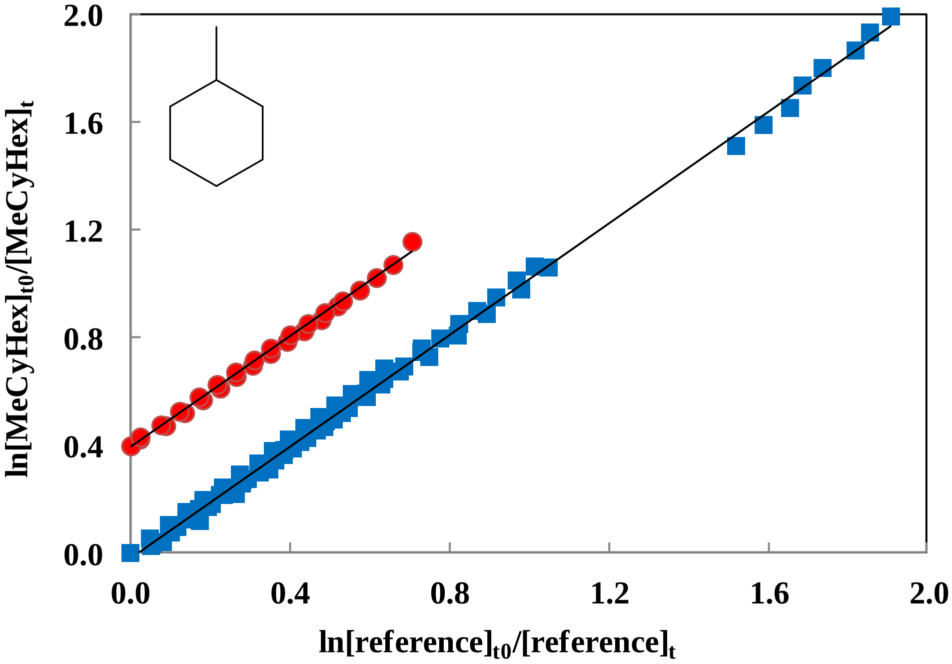

Figure S1. Plot of the kinetic data according to eq (3) for the reaction of Cl atoms with methylcyclohexane (MCH) using (●) trans-2-butene and (■) cyclohexane as the reference hydrocarbon. The data have been displaced vertically for clarity.

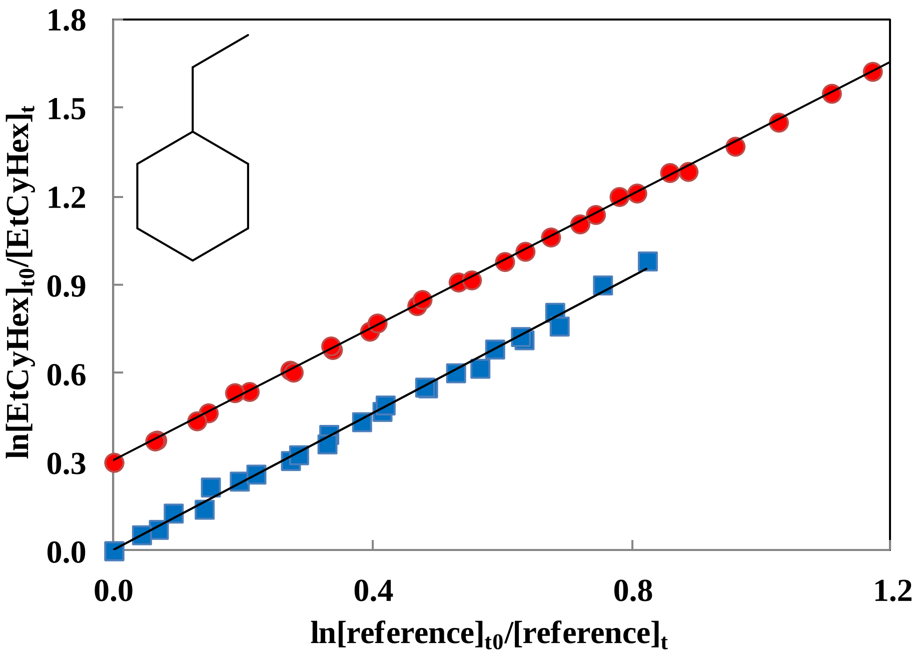

Figure S2. Plot of the kinetic data according to eq (3) for the reaction of Cl atoms with ethylcyclohexane (ECH) using (●) trans-2-butene and (■) cyclohexane as the reference hydrocarbon. The data have been displaced vertically for clarity.

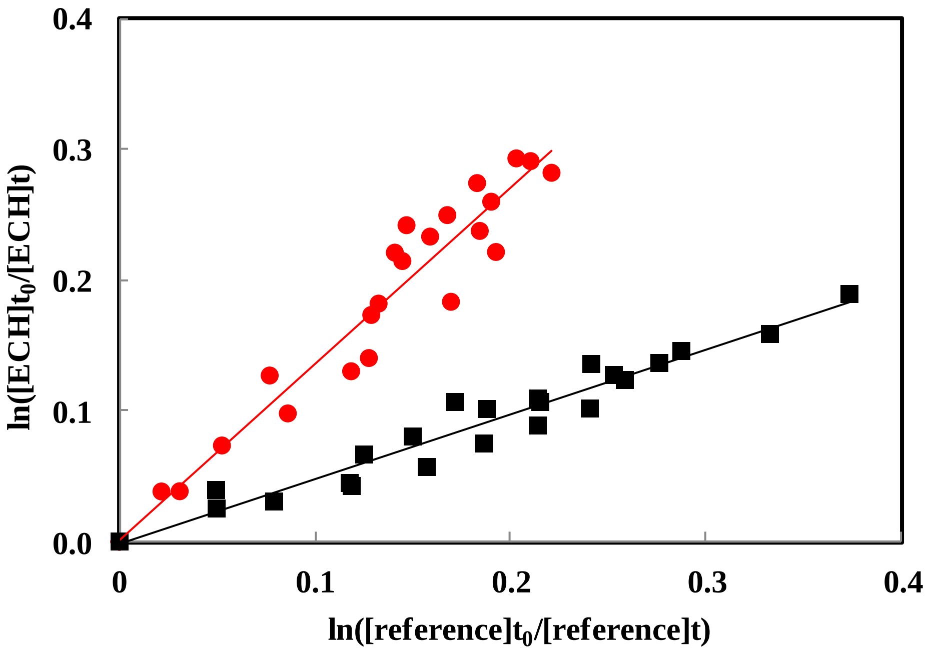

Figure S3. Kinetic data plotted according to eq (3) for the reaction of OH radicals with ECH performed in QUAREC chamber using propene (■) and ethene (●) as reference hydrocarbons.