

1. INTRODUCTION

Within the class of non methane hydrocarbons (NMHC), alkanes are the most common species emitted in urban atmosphere (42%). Their oxidation is the dominant source of Photochemical Ozone Creation Potential (POCP)-weighted emissions, 48% across Europe (Calvert et al., 2008). Cycloalkanes, widely used in solvents industry, are important components of diesel fuel derived from conventional crude-oil and oil-sand deposits. (Farrell et al., 2007). Cyclohexanes have the lowest total ring strain and are the most stable of the cycloalkanes. Cyclohexanes possess high and specific reactivity with OH, even more alkylated cyclohexane compounds are recommended as potential tracers for an indirect measurement of OH radicals.

In order to improve our knowledge of the atmospheric chemistry of alkylated cyclohexanes, we have investigated the kinetics of the reaction of OH radicals and Cl atoms with three alkylated cyclohexanes: methylcyclohexane, *trans*-1,4-dimethylcyclohexane and ethylcyclohexane.

However, the main aim of this study was to determine the temperature dependence of the rate coefficient for the reaction of methylcyclohexane with OH radicals in order to assess FAGE (Fluorescence Assay by Gas Expansion) instrument sensitivity to OH radical as a function of temperature. The hydrocarbon (methylcyclohexane) decay method will be used further as an alternative calibration method of FAGE instrument (Winiberg et al., 2014).

3. RESULTS: kinetics with Cl atoms

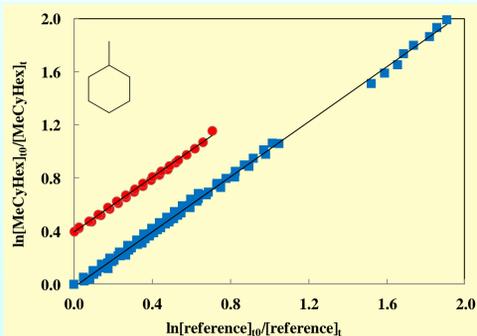


Fig. 2. Kinetic data plotted according to eq (1) for the reaction of Cl atoms with methylcyclohexane (MeCyHex) using *trans*-2-butene (●) and cyclohexane (■) as reference hydrocarbons. The data have been displaced vertically for clarity.

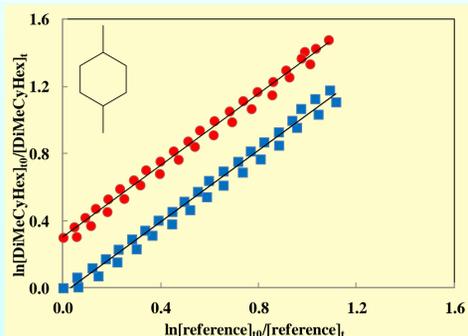


Fig. 3. Kinetic data plotted according to eq (1) for the reaction of Cl atoms with dimethylcyclohexane (DiMeCyHex) using *trans*-2-butene (●) and cyclohexane (■) as reference hydrocarbons. The data have been displaced vertically for clarity.

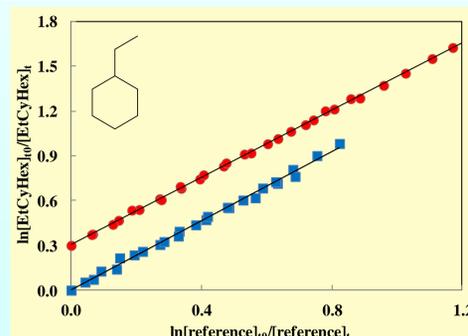


Fig. 4. Kinetic data plotted according to eq (1) for the reaction of Cl atoms with ethylcyclohexane (EtCyHex) using *trans*-2-butene (●) and cyclohexane (■) as reference hydrocarbons. The data have been displaced vertically for clarity.

Table 1. Rate coefficients for the reactions of Cl atom with three alkylcyclohexane compounds: methylcyclohexane (MeCyHex), 1,4-dimethylcyclohexane (DiMeCyHex) and ethylcyclohexane (EtCyHex). Cyclohexane $k(\text{CyHex}+\text{Cl})=3.30\pm 0.49 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2008) and *trans*-2-butene; $k(\text{trans-2-butene}+\text{Cl})=3.00\pm 0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Kaiser et al., 2007) have been used as reference compounds. For $\tau(\text{h})$, $[\text{Cl}] = 5 \times 10^4 \text{ cm}^{-3}$ (Spicer et al., 1998).
a) (Ballesteros et al., 2014).
b) (Aschmann and Atkinson, 1995).

Alkyl cyclohexane	reference	k_1/k_2	$k_1 \times 10^{10}$ [cm ³ .molec ⁻¹ .s ⁻¹]	$k_{\text{average}} \times 10^{10}$ [cm ³ .molec ⁻¹ .s ⁻¹]	$k_{\text{literature}} \times 10^{10}$ [cm ³ .molec ⁻¹ .s ⁻¹]	$k_{\text{SAR}} \times 10^{10}$ [cm ³ .molec ⁻¹ .s ⁻¹]	τ (h)
methyl cyclohexane	cyclohexane	1.04 ± 0.01	3.42 ± 0.52	3.51 ± 0.73	3.11 ± 0.16 ^a 3.47 ± 0.12 ^b	3.42	79.1
	<i>trans</i> -2-butene	1.03 ± 0.02	3.60 ± 0.52				
<i>trans</i> -1,4-dimethyl cyclohexane	cyclohexane	1.06 ± 0.04	3.51 ± 0.54	3.63 ± 0.77	2.89 ± 0.16 ^a	3.49	76.5
	<i>trans</i> -2-butene	1.07 ± 0.04	3.75 ± 0.55				
ethyl-cyclohexane	cyclohexane	1.16 ± 0.03	3.81 ± 0.58	3.88 ± 0.81		4.04	71.7
	<i>trans</i> -2-butene	1.13 ± 0.01	3.94 ± 0.56				

4. RESULTS: kinetics with OH radicals

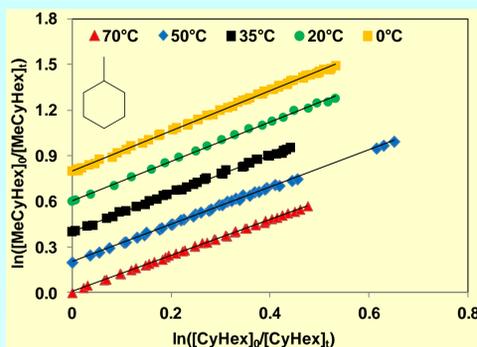


Fig. 5. Kinetic data plotted according to eq (1) for the reaction of OH radicals with MeCyHex at different temperatures using cyclohexane as reference hydrocarbon. The data have been displaced vertically for clarity.

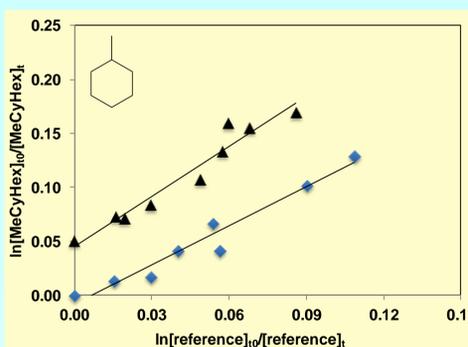


Fig. 6. Kinetic data plotted according to eq (1) for the reactions of OH radicals with MeCyHex using cyclohexane (●) and toluene (▲) as reference hydrocarbons.

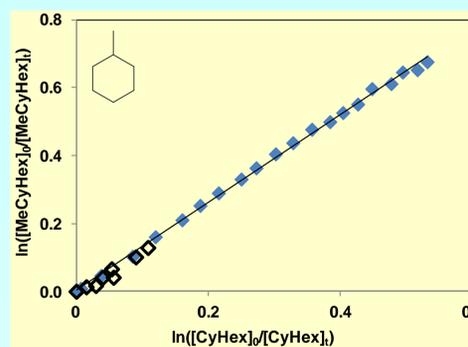


Fig. 7. Kinetic data plotted according to eq (1) for the reactions of OH radicals with MeCyHex using cyclohexane as reference hydrocarbons and two different sources of OH radicals: *trans*-2-butene ozonolysis (○) and CH₃ONO photolysis (●).

Table 2. Rate constants for the reactions of OH radicals with three alkylcyclohexane compounds in the temperature range 273 to 343 K. Reference hydrocarbons used in the study (in cm³ molecule⁻¹ s⁻¹) were: cyclohexane; $k(\text{cyclohexane}) = (3.62 \times 10^{-17}) \times T^2 \exp[(262)/T]$ (Atkinson, 2003) and toluene; $k(\text{toluene}) = 5.72 \times 10^{-12}$ (Calvert et al., 2002)
(^a) CH₃ONO photolysis as OH radical source, (^b) ozonolysis of *trans*-2-butene as OH radical source, (^c) only 20°C values

Alkyl cyclohexane	reference	k_1/k_2	$k_1 \times 10^{12}$ [cm ³ .molec ⁻¹ .s ⁻¹]	$k_{\text{average}} \times 10^{12}$ [cm ³ .molec ⁻¹ .s ⁻¹]	$k_{\text{literature}} \times 10^{12}$ [cm ³ .molec ⁻¹ .s ⁻¹]	$k_{\text{SAR}} \times 10^{12}$ [cm ³ .molec ⁻¹ .s ⁻¹]	τ (h)
methyl cyclohexane	cyclohexane ^a 0°C	1.32 ± 0.01	8.38 ± 0.11	8.62 ± 2.83 ^c	11.8 ± 1.2 ^c 11.1 ^d 9.4 ± 0.06 ^e 9.43 ^f	11.05	32.2
	cyclohexane ^a 20°C	1.29 ± 0.01	8.83 ± 0.21				
	cyclohexane ^a 35°C	1.32 ± 0.01	9.08 ± 0.15				
	cyclohexane ^a 50°C	1.32 ± 0.01	9.34 ± 0.13				
	cyclohexane ^a 70°C	1.32 ± 0.01	9.76 ± 0.10				
	cyclohexane ^b	1.21 ± 0.22	8.26 ± 2.22				
<i>trans</i> -1,4-dimethyl cyclohexane	cyclohexane ^b	1.23 ± 0.22	8.42 ± 1.89	6.86 ± 1.96	14.1 ± 1.5 ^c	13.7	40.5
	toluene ^b	0.93 ± 0.10	5.30 ± 0.55				
ethyl-cyclohexane	cyclohexane ^b	1.11 ± 0.03	7.59 ± 0.52	7.11 ± 0.56		12.2	39.07
	toluene ^b	1.16 ± 0.04	6.63 ± 0.47				

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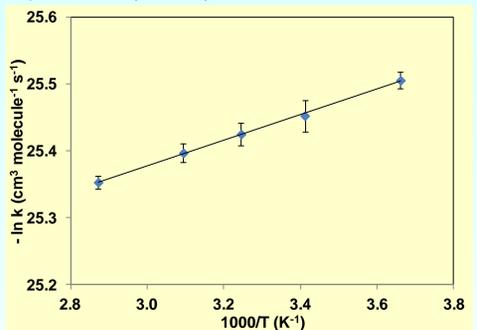


Fig. 8. Arrhenius plot of the rate constants for the reaction of OH radicals with MeCyHex (●) at five different temperatures.

Arrhenius expression for temperature dependent rate coefficient of MeCyHex + OH is (cm³ molec⁻¹ s⁻¹):

$$k_{(\text{MeCyHex} + \text{OH})} = (1.69 \pm 0.05) \times 10^{-11} \exp(-191.1 \pm 8.2)$$

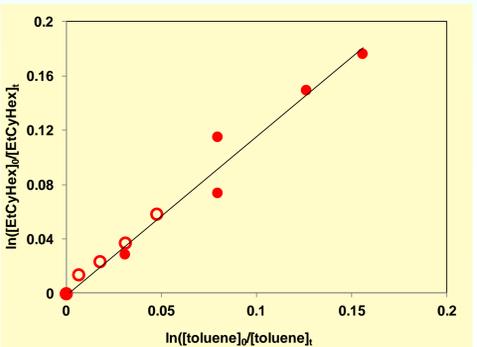


Fig. 9. Kinetic data plotted according to eq (1) for the reaction of OH radicals with EtCyHex using two different techniques to monitor reactant and reference compounds: FTIR (○) and GC-FID (●).

2. EXPERIMENTAL SETUP

HIRAC

Highly Instrumented Reactor for Atmospheric Chemistry

The kinetic measurements were performed in the HIRAC photoreactor. The chamber is described in detail elsewhere (Glowacki et al., 2007) (see Figure 1). A Chernin-type multiple reflection mirror system operated at a total optical path length of 128.52 m coupled to a BRUKER IFS/66 FTIR spectrometer and a GC-FID, equipped with a Varian Chrompack CP-Sil 5CB column (50 m, 0.32 mm i.d. and film thickness of 5 μm) were used for reactant and reference compound detection.

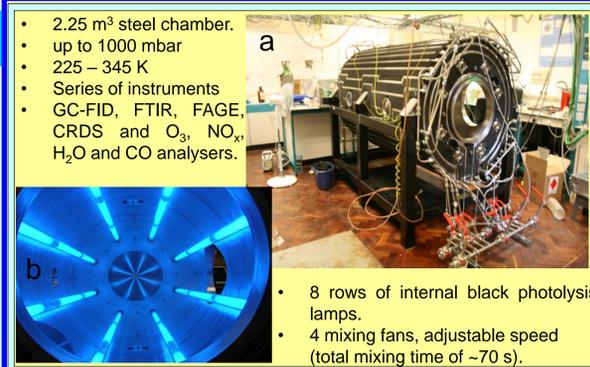


Fig. 1. a) HIRAC – external view; b) Inner view of the tubular HIRAC reactor with the photolysis lamps switched ON.

- 2.25 m³ steel chamber.
- up to 1000 mbar
- 225 – 345 K
- Series of instruments
- GC-FID, FTIR, FAGE, CRDS and O₃, NO_x, H₂O and CO analysers.

- 8 rows of internal black photolysis lamps.
- 4 mixing fans, adjustable speed (total mixing time of ~70 s).

OH kinetic

The photolysis of CH₃ONO with 8 blacklamps in the presence of air was used as the OH radical source:



Additionally, the ozonolysis of *trans*-2-butene has been used as OH source.

Cl kinetic

The photolysis of Cl₂ was used as the Cl atom source:



Relative rate kinetic

The experimental data are plotted in Figures 2 – 7 and 9 according to eq (1).



$$\ln \frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t} = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_{t_0}}{[\text{reference}]_t} \quad (1)$$

CH₃ONO (~3 ppmV), alkylcyclohexane (1.5-2.5 ppmV), Cl₂ (~10ppmV) were added into the reactor using vacuum line with a flow of nitrogen.

Five steps of *trans*-2-butene ozonolysis were performed in order to obtain 20-30% decay of the alkylcyclohexanes. O₃, 2 ppmv, has been added prior to addition of the reactants.

5. DISCUSSION

All the kinetic plots (Figure 2-7,9) show good linearity even considering the difficulties which arise studying OH radical initiated chemistry with OH radical obtained by ozonolysis of alkenes (*trans*-2-butene);

First reported kinetic rate coefficients of the reactions of OH radicals and Cl atoms with ethylcyclohexane;

First reported temperature dependent kinetic study (Figure 5, 8) of the reaction of OH radicals with methylcyclohexane at 1000 mbar of air using a relative method;

Very good agreement between the rate coefficients obtained using two different reference hydrocarbons for both Cl atom and OH radical initiated reaction chemistry (*trans*-2-butene and cyclohexane for Cl atom kinetic (Figure 2-4) and toluene and cyclohexane for OH radical kinetic (Figure 6 and 9));

For the rate coefficients in the temperature range of 273 – 343 K a positive temperature dependence for methylcyclohexane with OH radicals was observed (Fig. 8);

Good agreement have been obtained with the literature $k(\text{Cl})$ and $k(\text{OH})$ data for methylcyclohexane rate coefficients (Table 1 and Table 2);

Using two different techniques (FTIR and GC-FID) (Figure 9) for monitoring of the reactant (ethylcyclohexane) and reference hydrocarbon (toluene), very good agreement has been obtained.

The rate coefficients for the reaction with Cl atoms are close to the gas kinetic collision limit and thus the effect of the methylation of cyclohexanes is small.

The substitution of H by alkyl group (-CH₃, -C₂H₅) in cycloalkane increase the rate coefficient due to the faster H abstraction from tertiary C.

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