RESEARCH ARTICLE

Room temperature rate coefficients for the reaction of chlorine atoms with a series of volatile methylsiloxanes (L$_2$-L$_5$, D$_3$-D$_6$)

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Abstract

The kinetics of chlorine (Cl) atom reactions with a series of volatile methylsiloxanes (VMS) including hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) were investigated in relative rate experiments at room temperature and atmospheric pressure. The experiments were carried out in a 0.2 m^3 PFA Teflon chamber, employing proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) as the chemical-analytical tool. The following relative and absolute reaction rate coefficients were obtained using isoprene as reference compound ($k_{VMS}/k_{isoprene}$; $k_{VMS} \times 10^{10}$ cm^3 molec^{-1} s^{-1}): L2 (0.32 $\pm$ 0.02; 1.31 $\pm$ 0.21), L3 (0.38 $\pm$ 0.00; 1.56 $\pm$ 0.23), L4 (0.48 $\pm$ 0.01; 1.98 $\pm$ 0.29), L5 (0.54 $\pm$ 0.03; 2.22 $\pm$ 0.34), D3 (0.14 $\pm$ 0.02; 0.56 $\pm$ 0.13), D4 (0.26 $\pm$ 0.01; 1.05 $\pm$ 0.16), D5 (0.36 $\pm$ 0.02; 1.46 $\pm$ 0.22), D6 (0.39 $\pm$ 0.02; 1.61 $\pm$ 0.25). The following relative and absolute reaction rate coefficients were obtained using toluene as reference compound ($k_{VMS}/k_{toluene}$; $k_{VMS} \times 10^{10}$ cm^3 molec^{-1} s^{-1}): L2 (1.59 $\pm$ 0.18; 0.95 $\pm$ 0.14), L3 (2.25 $\pm$ 0.14; 1.35 $\pm$ 0.16), L4 (2.38 $\pm$ 0.01; 1.43 $\pm$ 0.14), L5 (3.57 $\pm$ 0.11; 2.14 $\pm$ 0.22), D3 (0.87 $\pm$ 0.01; 0.52 $\pm$ 0.05), D4 (1.48 $\pm$ 0.12; 0.89 $\pm$ 0.11), D5 (2.02 $\pm$ 0.15; 1.21 $\pm$ 0.15), D6 (2.54 $\pm$ 0.11; 1.52 $\pm$ 0.17). Our data confirm that reactions with Cl atoms need to be taken into account when assessing the decomposition of VMS in Cl-rich tropospheric environments.

KEYWORDS
atmospheric chemistry, volatile methylsiloxanes, Cl radical, relative rate measurement, PTR-ToF-MS

1 | INTRODUCTION

Volatile methylsiloxanes (VMS) are compounds consisting of -$(CH_3)_2SiO$-structural units in linear or cyclic arrangements that exhibit a relatively high vapor pressure. They are widely used as intermediates in the manufacture of silicone polymers and as ingredients in a range of cosmetics and personal care products. Due to their high volatility, the use of these chemicals leads to significant emission into the atmosphere. The range of linear and cyclic VMS found in the atmosphere includes hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) (Figure 1).[1,2,3,4]

Based on the pioneering work by Atkinson[5] and Sommerlade et al.[6], the gas-phase reaction with hydroxyl (OH) radicals was for a long time considered to be the only important tropospheric loss process for VMS. This was despite the fact that Atkinson et al.[7] had reported L2 reacting 100 times faster with chlorine (Cl) atoms than with OH radicals. Only after the systematic study by Alton and Browne[8] on the kinetics of the reaction between Cl atoms and L2, L3, L4, L5, D3, D4, D5, respectively, it was recognized that this breakdown pathway needs to be considered in Cl-rich tropospheric environments. A closer look at the data reported by Alton and Browne[8]; see Table 2 in that study) reveals that some of the rate coefficients have relatively large uncertainties. Given that this was the only systematic study hitherto carried out, we have performed an additional study using different reference compounds for relative rate determination. We also included D6 for the first time in the systematic kinetic work on Cl-VMS reactions.

2 | METHODS

2.1 | Kinetic experiments

The experiments were conducted in a 0.2 m^3 reaction chamber made of optically clear PFA Teflon (Welch Fluorocarbon Inc., Dover, New Hampshire, USA). The chamber
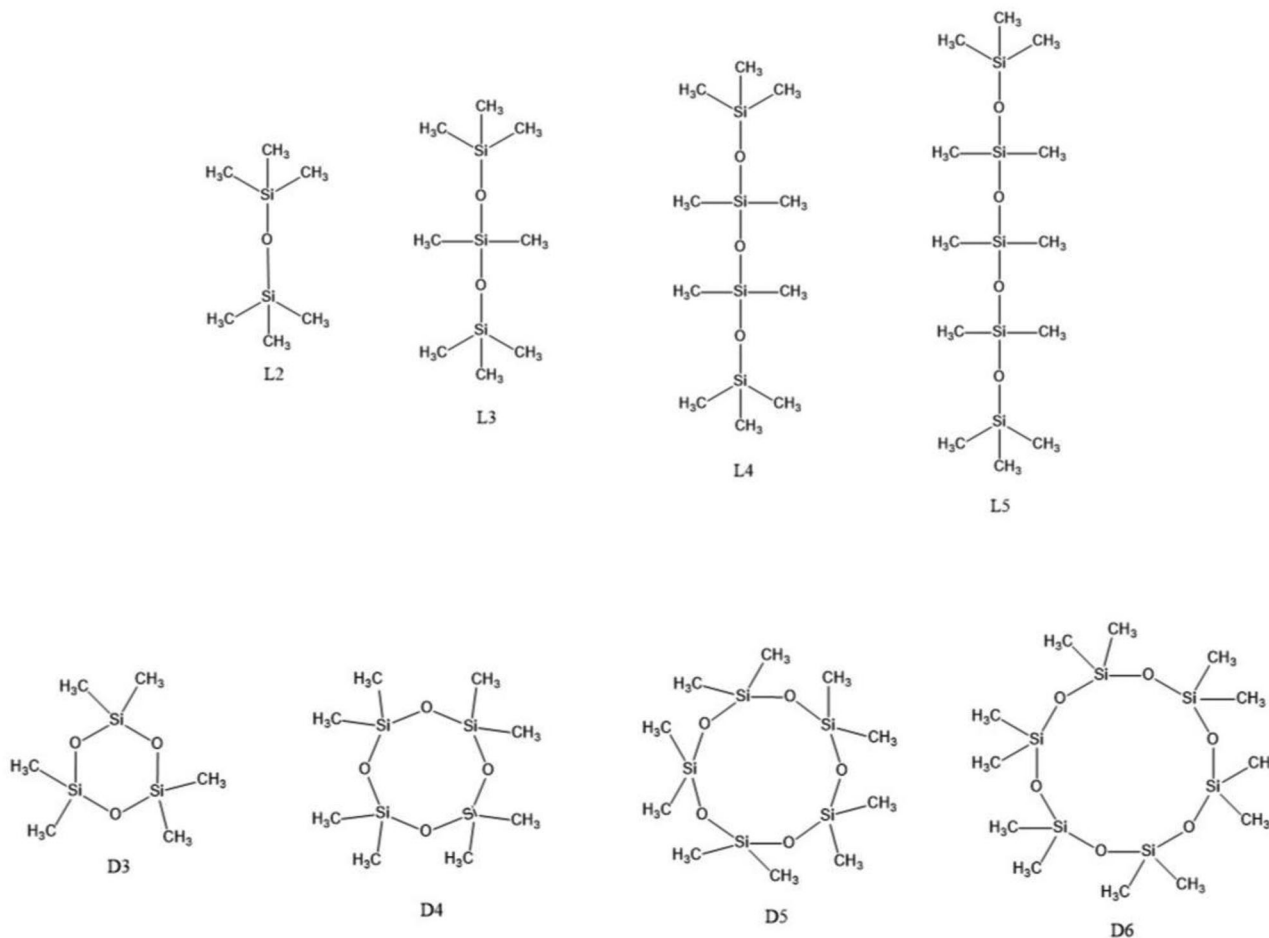

FIGURE 1 Chemical structure and short name of the volatile methylsiloxanes (VMS) investigated in this study.

had an inlet and an outlet port and was surrounded by four blacklight blue (BLB) lamps (2 × Philips TL-D 36 W BLB, 2 × Philips TL-D 18 W BLB; 340 nm < λ < 400 nm, λ_{max} = 365 nm). We first filled the chamber with ~50 L of synthetic air (5.0; Nippon Gases, Oslo, Norway) and then injected the reference compound, either isoprene (99%; Merck Life Science, Oslo, Norway) or toluene (99.7%; Merck Life Science, Oslo, Norway), through a septum into the airflow while further filling the chamber. Eight VMS were obtained from Merck Life Science and used without further purification: hexamethyldisiloxane (L2; 98.5%), octamethyltrisiloxane (L3; 98%), decamethyltetrasiloxane (L4; 97%), dodecamethylpentasiloxane (L5; 97%), hexamethylcyclotrisiloxane (D3; 98%), octamethylcyclotetrasiloxane (D4; 98%), decamethylcyclopentasiloxane (D5; 97%), and D6 dodecamethylcyclohexasiloxane (97%). The VMS were injected in a similar manner as the reference compounds. In the case of D3, which is a solid, an aliquot was evaporated under a synthetic air stream. Chlorine gas (7.4 ppm Cl_2 in N_2; Nippon Gases, Oslo, Norway) was first filled into a 2.25 L stainless steel cylinder at 1.5 bar and then flushed into the chamber in a flow of synthetic air. The nominal mixing ratios (not accounting for potential injection losses) of the VMS, the reference compound and molecular chlorine in the reaction chamber were 150, 50, and 120 ppb, respectively. The chamber was left to equilibrate for 30 min to check for potential wall losses. Neither the VMS nor the reference compounds exhibited any wall losses. Then the ultraviolet (UV) lamps were turned on and kept on for 1 h. Dissociation of molecular chlorine formed chlorine atoms, which resulted in a slow decay of the VMS and the reference compound. For analysis, we only used the initial phase of the decay (≤20% loss of the fastest reagent; typically the first 30–40 min of irradiation) to avoid any potential bias from confounding factors (e.g., secondary chemistry, slow adsorption/desorption of analytes). No decay was observed when the VMS were irradiated in the absence of chlorine. All experiments were carried out at atmospheric pressure. The gas volume extracted by the analytical instrumentation (see section 2.2) was not replenished, which led to a slow collapse of the reaction chamber. The experiments were carried out at room temperature (296 ± 2 K). After each experiment, the reagent mixture was pumped out and the chamber was flushed with clean air multiple times. All experiments were conducted in triplicate.

2.2 | Proton-Transfer-Reaction Mass Spectrometry

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a direct introduction chemical ionization mass spectrom-

etry technique that has been widely used in atmosphere simulation chamber experiments over the past 20 years.[9,10] For the work described herein, we used a PTR-TOF 4000 X2 instrument (Ionicon Analytik, Innsbruck, Austria) that was operated in the H_3O^+ mode at a reduced electric field strength of 100 Td (Td = Townsend, 1 Td = 10^{-17} V cm^{-2}). The instrument continuously sampled air from the reaction chamber at a flow rate of 100 standard cubic centimeters per minute (sccm; "standard" herein means referenced to a temperature of 273.15 K and a pressure of 101325 Pa). The VMS were monitored in their protonated form: m/z 163.097 (L2), m/z 237.116 (L3), m/z 311.134 (L4), m/z 385.153 (L5), m/z 223.064 (D3), m/z 297.082 (D4), m/z 371.101 (D5), m/z 445.120 (D6). The reference compounds isoprene and toluene were also monitored in their protonated form at m/z 69.070 and m/z 93.070, respectively. None of the analytes were calibrated, since the relative rate method (see section 2.3) does not require the use of absolute analyte concentrations. At the given operating conditions, the instrumental response to toluene exhibited a slight humidity dependence. This was corrected for in the data analysis, as water desorption from the Teflon film and/or permeation through the Teflon film slightly increased the humidity in the chamber during the course of the 1-h experiment. The resulting signal change was less than 3%. The VMS and isoprene did not exhibit a humidity dependent response.

2.3 | Data analysis

The Cl reaction rate coefficients of the siloxanes were determined using the relative rate method, that is by considering two competing bimolecular reactions with the rate coefficients k_{VMS} and $k_{Reference}$:

$$VMS + Cl \xrightarrow{k_{VMS}} products$$

$$Reference + Cl \xrightarrow{k_{Reference}} products$$
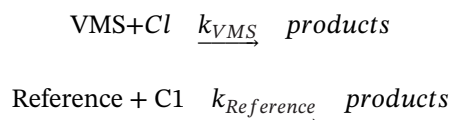
Assuming that there are no other loss processes for the VMS and the reference compound, the following relation can be obtained:

$$\ln\left(\frac{[VMS]_0}{[VMS]_t}\right) = \frac{k_{VMS}}{k_{Reference}} \ln\left(\frac{[Reference]_0}{[Reference]_t}\right)$$

where $[VMS]_0$ and $[Reference]_0$ are the concentrations of the VMS and the reference compound at time t = 0, respectively, and $[VMS]_t$ and $[Reference]_t$ are the concentrations at time t. Plots of the measured $\ln([VMS]_0/[VMS]_t)$ versus the measured $\ln([Reference]_0/[Reference]_t)$ yields a straight line with the slope describing the relative rate $k_{VMS}/k_{Reference}$. We used the reduced major axis regression

(RMA) method for deriving the slope, because the two measurement variables and their errors are independent. The intercept was not forced through zero.

As mentioned above, we used isoprene and toluene as reference compounds. Based on the latest NASA/JPL review[11], the room temperature rate coefficient for the Cl + isoprene reaction is $4.10 \pm 0.6 \times 10^{-10}$ cm^3 molec^{-1} s^{-1}. Calvert et al.[12] give a representative rate coefficient (298 K) for the Cl + toluene reaction of $0.6 \pm 0.06 \times 10^{-10}$ cm^3 molec^{-1} s^{-1}.

The uncertainty of the relative rate coefficients reported herein is the standard deviation (SD, 1σ) of the slopes determined in three experiments. The uncertainty of the absolute rate coefficients reported herein includes the uncertainty of the relative rate coefficients and the uncertainty of the absolute rate coefficients of the reference compounds.

3 | RESULTS AND DISCUSSION

The relative rate plots obtained when isoprene was used as the reference compound are shown in Figure 2. We note that kinetic experiments were conducted with only one VMS and the reference compound being present in the Teflon chamber, meaning that each figure contains data from four separate experiments. We reiterate that we only used data from the initial phase of the reaction for our analysis (see Methods). The relative rate plots show very good linearity. The uncertainty in the slope derived from a single experiment (not reported) was typically much smaller than the SD of the slopes observed in the triplicate experiments. Forcing the intercept through zero typically changed the slope by less than 3% (6% in one instance), which is again much smaller than the SD of the slopes observed in the triplicate experiments. These small additional uncertainties were not considered in the further analysis. The slopes of the regression lines, which were obtained using the RMA method (see Methods), are the relative rate coefficients.

The relative rate plots obtained when toluene was used as the reference compound are shown in Figure 3. The relative rate plots again show very good linearity.

Since experiments were carried out in triplicate, we calculated the mean and the SD (1σ) for all derived slopes. The resulting relative rate coefficients ($\pm$SD) are summarized in Table 1. The table also includes the absolute rate coefficients, which were derived using a rate coefficient of $0.6 \pm 0.06 \times 10^{-10}$ cm^3 molec^{-1}s^{-1} [12] for the Cl + toluene reaction and a rate coefficient of $4.10 \pm 0.6 \times 10^{-10}$ cm^3 molec^{-1}s^{-1} [11] for the Cl + isoprene reaction. The uncertainty in the absolute rate coefficients includes the uncertainty of the slope and the uncertainty
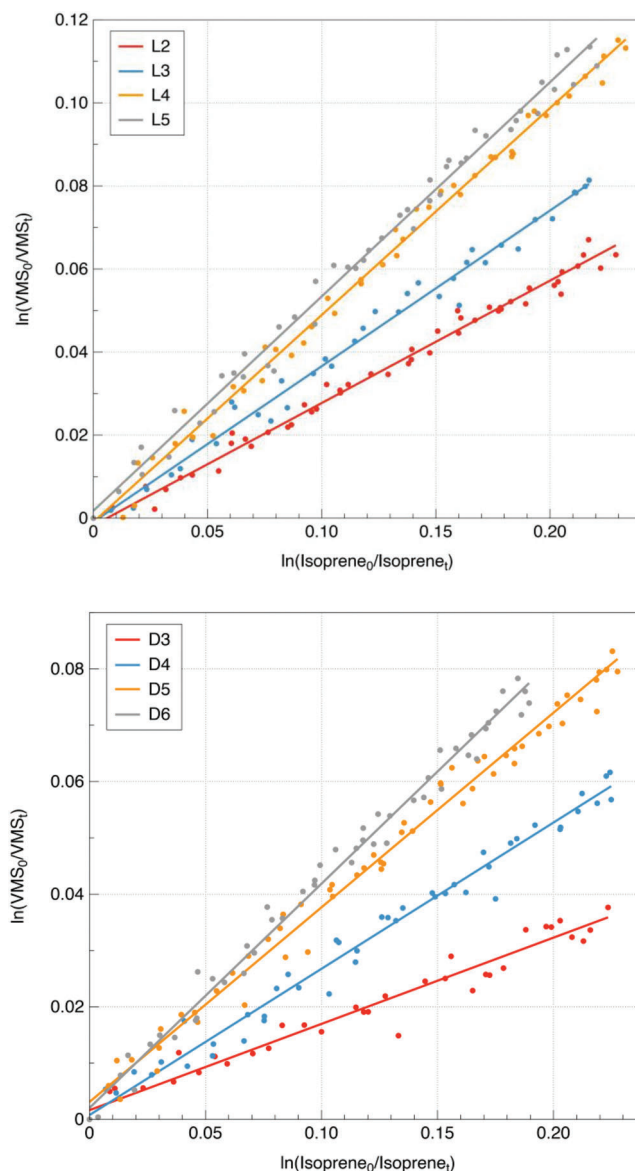

FIGURE 2 Relative rate plots for the reaction of Cl atoms with a series of VMS and isoprene as the reference compound.

of the absolute reaction rate coefficient of the reference compound. The latter is the major contributor to the uncertainty.

In Figure 4, we plot the absolute rate coefficients derived from our study (reference compounds: toluene and isoprene) together with the literature values form Atkinson et al.[7] (reference compound: n-butane) and Alton and Browne[8] (reference compounds: methylethylketone (MEK) and diethyl ether). For deriving the Atkinson et al.[7] data point, we used the currently recommended rate coefficient of $2.05 \pm 0.30 \times 10^{-10}$ cm^3 molec^{-1}s^{-1}[13] for the Cl + n-butane reaction. We have adapted the uncertainties in the literature values to include the uncertainty of the slope and the uncertainty of the absolute reaction rate coefficient of the reference compound (as reported in their
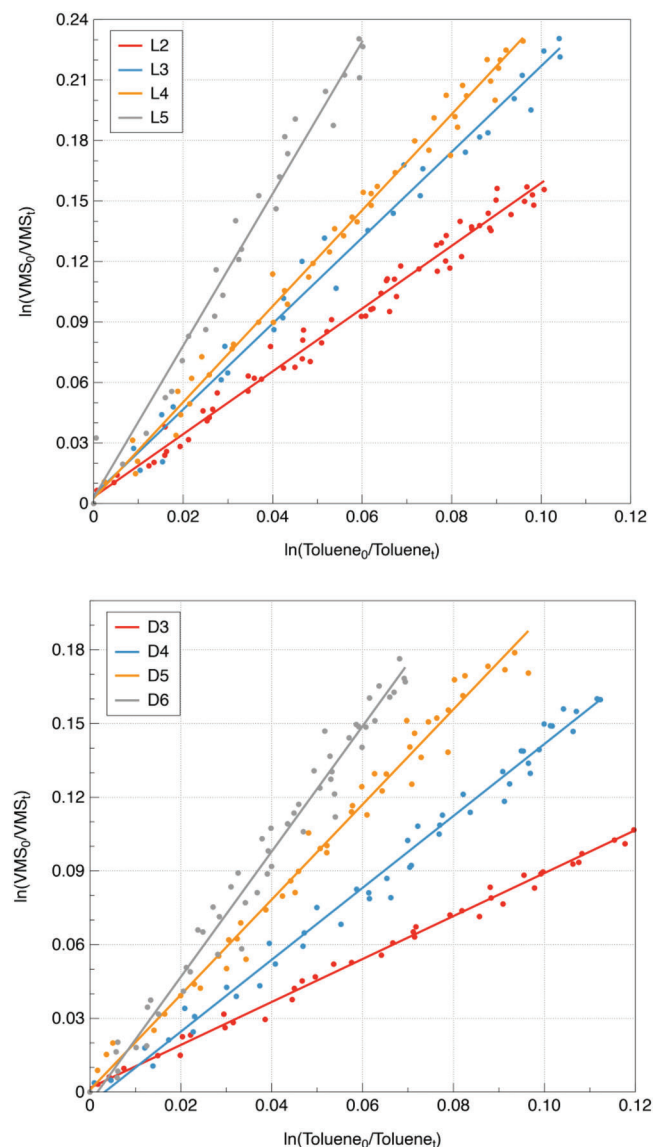
FIGURE 3 Relative rate plots for the reaction of Cl atoms with a series of VMS and toluene as the reference compound.

studies). We note that Atkinson et al.[7] and Alton and Browne[8] reported 2σ uncertainties, while our values have 1σ uncertainties.

We first discuss the results from our study. The absolute rate coefficients obtained from the reference compound toluene are always smaller than the rate coefficients obtained when using isoprene as the reference compound. The results do, however, agree to within the combined uncertainties. The only exception is the rate coefficient for Cl-L4 reaction, for which we obtained a 28% lower value when using toluene as the reference compound. We still regard this as a satisfactory agreement.

The absolute rate coefficients reported by Alton and Browne[8] are higher than our values for the larger VMS (L3, L4, L5, D4, D5). As mentioned in the introduction, some values from this previous study have a relatively large uncertainty. They do agree to within the combined uncertainties with our isoprene-derived absolute rate coefficients. Our toluene-derived absolute rate coefficients were up to 38% lower than the Alton and Browne[8] data. One exception is the Cl-D3 reaction, for which our and the literature values are in excellent agreement. This finding suggests that the observed discrepancies are not attributable to errors in the absolute reactions rate coefficients of the reference compounds. We note that the spread in the Cl rate coefficients is similar to the spread in the siloxane + OH rate coefficients (see Figure 2 of Alton and Browne[8]).

Figure 5 shows that rate coefficient of the reaction of Cl atoms with VMS linearly increases with the number of methyl groups in the reagent VMS. This can be easily explained by the fact that the probability for a Cl atom abstracting a hydrogen atom from a methyl group increases linearly with the number of methyl groups. Linear and cyclic VMS exhibit the same linear trend (within the uncertainty of the slope). This contradicts the finding of Alton and Browne[8] who reported the rate coefficients of cyclic VMS to increase faster than those of linear VMS.

TABLE 1 Relative and absolute reaction rate coefficients obtained in this study

	Reference compound: toluene		Reference compound: isoprene	
	$k_{VMS}/k_{reference}$	$10^{10} \times k_{VMS}$ (cm^3 molec^{-1}s^{-1})	$k_{VMS}/k_{reference}$	$10^{10} \times k_{VMS}$ (cm^3 molec^{-1}s^{-1})
L2	1.59 ± 0.18	0.95 ± 0.14	0.32 ± 0.02	1.31 ± 0.21
L3	2.25 ± 0.14	1.35 ± 0.16	0.38 ± 0.00	1.56 ± 0.23
L4	2.38 ± 0.01	1.43 ± 0.14	0.48 ± 0.01	1.98 ± 0.29
L5	3.57 ± 0.11	2.14 ± 0.22	0.54 ± 0.03	2.22 ± 0.34
D3	0.87 ± 0.01	0.52 ± 0.05	0.14 ± 0.03	0.56 ± 0.13
D4	1.48 ± 0.12	0.89 ± 0.11	0.26 ± 0.01	1.05 ± 0.16
D5	2.02 ± 0.15	1.21 ± 0.15	0.36 ± 0.01	1.46 ± 0.22
D6	2.54 ± 0.11	1.52 ± 0.17	0.39 ± 0.02	1.61 ± 0.25

FIGURE 4 Absolute rate coefficients of the reaction of Cl atoms with a series of VMS as obtained from this study and reported in two previous studies.
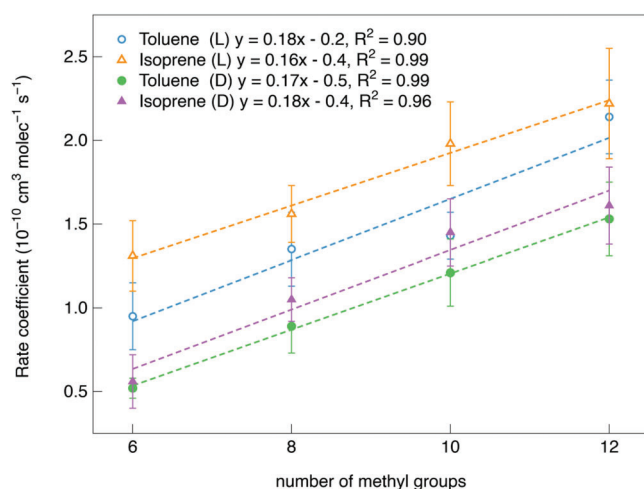
FIGURE 5 Reaction rate coefficients of the reaction of Cl atoms with a series of VMS plotted as a function of the number of methyl groups in the VMS.

4 | CONCLUSIONS

We have derived the rate coefficients of Cl atoms with a series of linear and cyclic VMS (L2, L3, L4, L5; D3, D4, D5, D6) at room temperature (296 ± 2 K) and atmospheric pressure making relative rate measurements against toluene and isoprene. The results obtained from the two reference compounds are in reasonably good agreement, and our values compare reasonably well with the data reported by Atkinson[7] and Alton and Browne[8]. For some compounds, we did, however, observe discrepancies up to 30% or even 40%, which is beyond the combined uncertainties of the different measurements. Our data confirm the results by

Alton and Browne[8] who found that Cl-VMS reactions need to be considered in Cl-rich tropospheric environments. A reaction rate coefficient of $\sim 2 \times 10^{-10}$ cm^3 molec^{-1}s^{-1} (as observed for the larger VMS) results in a lifetime between 14 and 140 h, respectively, for Cl atom concentrations in the range between 10^4 and 10^5 cm^{-3}. Such Cl atom concentrations have been observed in the polluted urban environment and marine boundary layer.[14,15] Our data add to the scarce literature on the Cl-VMS reaction kinetics, with the Cl-D6 reaction rate coefficient being reported for the first time.

CONFLICT OF INTEREST STATEMENT
The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT
None.

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