

Rate coefficients for the gas-phase reaction of the OH radical with L₂, L₃, D₃, and D₄ methylsiloxanes measured between 240 and 370 K

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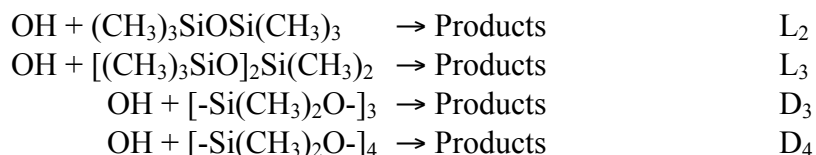
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The atmospheric chemistry of organosiloxanes has recently been implicated in the formation of new particles (Wu and Johnston, 2016) as well as regional and indoor air quality (Genualdi et al, 2011; Yucuis et al., 2013; Tang et al., 2015). Methylsiloxanes with Si<6 are relatively volatile compounds with either linear or cyclic molecular structures. Methylsiloxanes are found in consumer goods such as cosmetics, textiles, health care and household products and in industrial applications as solvents and lubricants. They are released into the atmosphere during manufacturing, use, and disposal and have been observed in the atmosphere in ppb levels in certain locations. However, the fundamental chemical properties of this class of compounds, particularly their reactivity with the OH radical, are presently not fully characterized.

In this work, the temperature dependence of the rate coefficients for the OH radical reaction with the simplest linear (L₂ and L₃) and cyclic (D₃ and D₄) siloxanes were measured:



OH rate coefficients were measured under pseudo-first conditions in OH over the temperature range 240–370 K using a pulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique. Complementary relative rate measurements were also performed at 294 K and the results were found to be in good agreement with the absolute results. The linear siloxanes were more reactive than the cyclic compounds studied here, while the OH reactivity for linear and cyclic compounds increased with increasing number of methyl groups. For L₂, D₃, and D₄ a positive Arrhenius temperature dependence was observed, while for L₃ a slight non-Arrhenius behavior was observed over the range of temperatures included in this study. The present results are compared with the available literature data where possible and discrepancies are discussed. The results from this work will be discussed in terms of the atmospheric lifetimes of these methylsiloxanes and the reactivity trends for this class of compound in general.

References

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