

Second Order Rate Constants for the Gas Phase Reactions of Cyclic (D3-D5) and Linear (L2-L4) Siloxanes with Hydroxyl Radicals Measured using a Relative Rate Method.

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Volatile methylsiloxanes (VMSs) are anthropogenic compounds commonly used as carriers in a number of cosmetic products as well as intermediates in the production of silicones.¹ Being volatile, the distribution and fate of VMSs in the environment is largely determined by their persistence in the atmosphere. We measured the rate constant for the reaction of linear and cyclic VMSs with the dominant oxidant in the stratosphere, hydroxyl radicals,² using a relative rate method. Our measurements were conducted using a mass spectrometer that was modified for on-line sampling of a custom-built small-scale (140 mL) reaction chamber in which hydroxyl radicals were produced *in situ* by the reaction of ozone with water under UV irradiation. We compared reaction kinetics and precision of measurements for the VMSs in experiments using a suite of commonly used reference compounds, and selected 2,2,4-trimethylpentane and cyclohexane as a reference compound for the cyclic and linear VMSs respectively.

We measured the rate constants at a range of temperatures from 40 °C to 90 °C. Extrapolated rate constants at 25 °C (298 K) for linear (L) and cyclic (D) VMSs are:

Compound	L2	L3	L4	D3	D4	D5
Rate Constant $k \times 10^{12}$ at 298 K (cm ³ molecule ⁻¹ s ⁻¹)	1.44	2.40	3.34	1.85	2.34	2.55

Arrhenius plots demonstrated that the temperature dependence of the reaction was weak for the linear VMSs, and that reaction rates are slightly higher at higher temperatures; all linear VMSs have positive activation energies in the range of 5-6.5 kJ/mol. In contrast, the activation energies of the cyclic siloxanes increase with molecular weight. D3 is particularly unusual in that it has a negative activation energy of -12 kJ/mol. Thus, the rate of reaction of D3 is slower at higher temperatures and the rate is about twice as sensitive to changes in temperature as the reaction rates of linear siloxanes. The trends in activation energies for the gas phase reactions of the cyclic VMS with OH are correlated with differences in molecular geometries determined from molecular modelling, and thus differences in the reactivity of hydrogens in the different VMS structures may be a potential explanation for the trends in activation energies.

1. Alleni, R. B.; Kochs, P.; Chandra, G., *Industrial Organosilicon Materials, Their Environmental Entry and Predicted Fate*. Springer Berlin Heidelberg: 1997; Vol. 3 / 3H.
2. Atkinson, R.; Arey, J., Atmospheric Degradation of Volatile Organic Compounds. *Chemical Reviews* **2003**, 103 (12), 4605-4638.