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Temperature dependence of the reactions between a series of alcohols and Cl atoms

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Atomic chlorine is highly reactive with organic and inorganic compounds, so that relatively small concentrations can compete with the main tropospheric oxidants (OH, O_3 and NO_3), playing a more important role in the oxidation of volatile organic compounds (VOCs), including the studied alcohols, than previously thought (Finlayson-Pitts, 1993). The contribution of Cl to the oxidation of VOCs could be significant in areas where the concentration of Cl precursor species has been reported to be high, such as coastal boundary layer, and it may significantly contribute to the formation of ozone and other components of the photochemical smog in these areas.

Absolute rate coefficients have been measured for the gas phase reactions of chlorine atoms with a series of aliphatic alcohols: methanol (k_1), ethanol (k_2), 1propanol (k_3), 1butanol (k_4) and 1pentanol (k_5), using the Pulsed Laser Photolysis – Resonance Fluorescence technique (PLP-RF), over the temperature range 264-382 K. The obtained kinetic data were used to derive the Arrhenius expresions: k_1 = (3.55 $\pm$ 0.22) $\times$ 10^{-10} exp[-(559 $\pm$ 40)/T]; k_2 = (5.25 $\pm$ 0.52) $\times$ 10^{-11} exp[(190 $\pm$ 68)/T]; k_3= (2.63 $\pm$ 0.21) $\times$ 10^{-11} exp[(525 $\pm$ 51)/T]; k_4= (3.12 $\pm$ 0.31) $\times$ 10^{-11} exp[(548 $\pm$ 65)/T] and k_5= (3.97 $\pm$ 0.48) $\times$ 10^{-11} exp[(533 $\pm$ 77)/T] (in units cm^3 molecule^{-1} s^{-1}).

As far as we know, the results from this work constitute the first temperature dependence measurements for the reactions of Cl with the mentioned alcohols, except for 1propanol. These rate coefficients will be compared with the previous studies carried out at 298 K (Wu, 2003), and with the reactivity of OH radicals (Wu, 2003; Jiménez, 2003). The atmospherics implications will be also discussed.

0.0.1 References

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