Trends in the rate coefficients of Cl atom reactions with cyclic molecules– A comparison between cyclic ethers and hydrocarbons

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The reactions of Cl atoms with VOCs contribute to the tropospheric chemistry of marine boundary layer and polluted coastal / non-coastal urban atmosphere. The reaction mechanism is very similar to that of OH radical, involving mainly abstraction of H atom, along with addition reactions in the case of unsaturated molecules. Generally, the reactivity of both OH and Cl towards unsaturated molecules is higher than that of the saturated ones, due to the higher rate coefficients of addition reactions. However, our recent measurement of rate coefficients of Cl atom reactions with unsaturated cyclic hydrocarbons at 298 K [1,2] showed an increase with number of carbon atoms (from 5-8), but no significant change with unsaturation. To further understand these trends as compared to that of OH radical reactions, rate coefficients of reaction of Cl atom with cyclic ethers, including one with unsaturation, are measured at 298 K using relative rate method.

The molecules studied are tetrahydropyran (THP), tetrahydrofuran (THF) and 2,5-dihydrofuran (DHF). These cyclic ethers are known to react very fast with OH radicals, their reactivity being higher than that of the corresponding hydrocarbons. The recent relative rate measurements of the rate coefficients of reactions of Cl atoms with THP and THF show the reactivity of THP to be lower than that of THF in spite of increased number of CH_2 groups, and no clear trend is observed in the reactivity of Cl atoms with the corresponding hydrocarbons [3].

The present measurements on THP and THF are carried out with reference to n-pentane, n-hexane and 1-butene, which are different from the reference molecules used in the previous reports. The relative ratios are not affected by the presence of oxygen. The average values of the rate coefficients are (2.52 ± 0.36), (2.52 ± 0.38) and (4.48 ± 0.59) x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for THP, THF and DHF, respectively. The rate coefficients for THP and THF agree well with the earlier reports and confirm that there is no increase in the rate coefficient of THP as compared to that of THF. It is also observed that unlike cyclic hydrocarbons, there is an increase in the rate coefficients with unsaturation in the ring. While the logarithmic values of the rate coefficients of OH reactions with cyclic hydrocarbons and ethers together correlate very well with HOMO energy, it is not found to be satisfactory in the case of rate coefficients of Cl atom reactions. The rate coefficients of Cl atom reactions, approaching collision controlled limits, do not correlate well with molecular size either when both hydrocarbons and ethers are considered together.

THURSDAY

References

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