Atmospheric Chemistry of Allyl Halides: Temperature and Pressure Dependent Rate Coefficients for the Gas Phase Reactions of OH Radicals and Cl Atoms with X-$CH_2CH=CH_2$ (X: Cl, Br, I)

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Two complementary experimental techniques were employed, in this work, to study the kinetics and the mechanism for the gas phase reactions of the major atmospheric oxidants, OH radicals and Cl atoms, with an allyl halides series, X-$CH_2CH=CH_2$ (X:Cl, Br and I), as a function of temperature (258 -365 K) and pressure (2×10^{-3} – 700 Torr). In particular, the zero pressure limit (~2 mTorr) rate coefficients for the Cl reactions were measured using the continuous-flow absolute rate method of Very Low Pressure Reactor (Knudsen Cell), coupled with quadrupole mass spectrometry (VLPR/QMS),[1] at T = 298 K. The OH and Cl pressure dependent rate coefficients (25 – 700 Torr) were measured employing the static relative rate method of the Thermostated PhotoChemical Reactor equipped with Fourier Transformed InfraRed Spectroscopy (TPCR/FTIR),[2] in the temperature range 260 – 365 K. Products were monitored with both FTIR spectroscopy and Mass spectrometry, and it was revealed that the association mechanism dominates over the potent abstraction reaction pathways, in consistence with the observed pressure (Cl reactions) and inverse to temperature dependence (both Cl and OH reactions) rate coefficient measured in the present study. Finally, IR cross sections were also determined and the Global Warming Potentials (GWP) of the studied allyl halides were estimated employing Pinnock model,[3] in a 20 years time-horizon, using rate coefficients and cross section measured in this work.

References

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