Kinetics of the atmospheric oxidation reaction of isoprene studied by pulsed laser photolysis / vacuum ultraviolet laser-induced fluorescence spectroscopy technique

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Isoprene is, by far, the most dominant volatile organic compound emitted into the Earth's atmosphere. Forests and plants emit approximately 500 TgC yr^{-1} of isoprene, while the combined emission of all volatile compounds from global transportation (land, water, and air) is approximately 22 TgC yr^{-1} [1]. A detailed understanding of the atmospheric oxidation mechanism of isoprene is clearly an important input for global atmospheric models. The atmospheric oxidation of isoprene is initiated by reaction with OH radicals, NO_3 radicals, and ozone. During daylight hours OH radicals likely dominate, while during nighttime the NO_3 radical is important. Evidence of relatively high concentrations of Cl atoms in the lower troposphere has prompted suggestions of the potential importance of Cl-initiated oxidation of isoprene.

To improve our understanding of the kinetics of Cl-initiated oxidation of isoprene, we employed absolute and relative rate methods to study this reaction in 1-700 Torr of N_2 and argon diluent [2]. Absolute rate measurements were made using pulsed laser photolysis / vacuum ultraviolet laser-induced fluorescence techniques (PLP/VUV-LIF). Relative rate measurements were made using smog chamber / FT-IR techniques. All experiments were performed at 297 ± 2 K. In the PLP/VUV-LIF experiments, gas mixtures of Cl_2 and isoprene diluted in N_2 or Ar were flowed through the reaction chamber. An excimer laser operating in a XeF mode generated 351 nm light to initiate the isoprene + Cl reaction through the photolytic production of Cl atoms from Cl_2 molecules. $Cl(^2P_{3/2})$ atoms were detected by VUV-LIF at 134.72 nm at $3p^5 \, ^2P_{3/2} - 4p^4 4s \, ^2P_{3/2}$ transition. Tunable coherent VUV radiation was generated by four-wave difference frequency mixing in Kr using two dye lasers pumped by a XeCl excimer laser.

Results are graphically shown in Figure 1 with available literature data. Our results are in good agreement with the previous absolute rate studies, but lie systematically lower than the results from most previous relative rate investigations in 1-700 Torr. The simplest explanation for the scatter of the relative rate data, and the fact that the relative rate data generally are above the absolute rate data in Fig. 1, is that formation of OH radicals is a complication in relative rate studies conducted in the presence of oxygen. The previous relative rate studies were conducted either in air, or in air and N_2 diluents. Peroxy radicals will be formed during the chlorine atom initiated oxidation of isoprene and the reference compounds used in previous relative rate studies conducted in air. It has been shown recently that the reactions of peroxy radicals with HO_2 radicals can generate OH radicals. The formation of OH radicals will lead to an overestimation of k(Cl+isoprene) in relative rate experiments conducted in air. For the purposes of representing the chemistry of isoprene in atmospheric models we recommend a pressure independent value of k(Cl+isoprene) = (3.44 ± 0.32) × 10^{-10} cm^3 molecule^{-1} s^{-1} based upon the present work.

References

[1] G. P. Brasseur, J. J. Orlando, G. S. Tyndall, Atmospheric Chemistry and Change, Oxford University Press, 1999.

[2] J.-H. Xing, K. Takahashi, M. D. Hurley, and T. J. Wallington, Kinetics of the reaction of chlorine atoms with isoprene (2-methyl 1,3-butadiene, $CH_2=C(CH_3)CH=CH_2$) at 297 ± 2 K, *Chem. Phys. Lett.*, 472, 39-43, 2009.

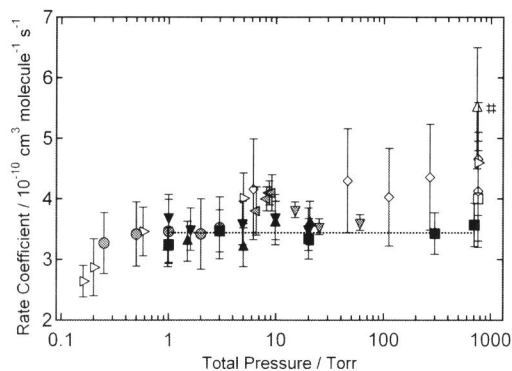
Figure 1 Rate coefficient k(Cl+isoprene) at 297±2K. Our data are shown in filled marks. The dotted line is the average value from our work at 1-700 Torr.