

Kinetic investigations on the OH radical and Cl atom initiated photo-oxidation reaction with 2,3-dimethyl-1,3-butadiene in troposphere: Experimental and computational studies

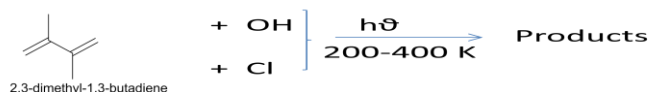
S. Vijayakumar and B. Rajakumar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.

*Address for correspondence: rajakumar@iitm.ac.in

Abstract:

The photo-oxidation of butadienes plays a significant role in the formation of Secondary Organic Aerosols (SOAs) under both low and high NO_x (nitrogen oxides) environments ^[1]. The hydroxyl radical initiated oxidation of butadienes establishing the balance of hydrogen oxides (HO_x= OH + HO₂) and influences the urban ozone formation in vegetated area where biogenic emissions are very high ^[2]. These butadienes are being released into the atmosphere due to incomplete combustion of gasoline, diesel fuels, auto mobile exhausts, areas close to the plastic or rubber industries, petroleum refining and subsequent industries etc ^[3]. The kinetic data and complete atmospheric degradation pathways of individual compounds are essential to reliably assess the possible contribution of these substances to the air pollution and climate change.



Temperature dependent rate coefficients were measured for the reactions of 2,3-dimethyl-1,3-butadiene with hydroxyl radicals and chlorine atoms over the temperature range of 263-363K by using Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF) and Relative Rate (RR) experimental techniques. Measured rate coefficients were used to fit the Arrhenius equations and are $k_{2,3\text{-dimethyl-1,3-butadiene+OH}}(269\text{-}363\text{K}) = (1.92 \pm 0.46) \times 10^{-11} \exp[(490.19 \pm 76.23)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{2,3\text{-dimethyl-1,3-butadiene+Cl}}(269\text{-}363\text{K}) = (4.59 \pm 0.78) \times 10^{-11} \exp[(676.14 \pm 52.8)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To deeper insight the reaction mechanism and to complement our experimental results, computational calculations were performed over the temperature range of 200-400K for title reactions using Canonical Variational Transition state theory (CVT) in combination with QCISD(T), CCSD(T)/aug-cc-pVDZ, MP2/6-31+G(d,p) level of theories. Atmospheric implications and thermodynamic parameters of the test molecule will be discussed in detailed in the conference.

References:

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