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Kinetics Study and Atmospheric Degradation of *n*-Butyraldehyde by Hydroxyl Radicals

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Extended Abstract

Carbonyl compounds play a crucial role in atmospheric chemistry and urban air pollution. They are emitted from both biogenic and anthropogenic sources and are also formed in situ through the photooxidation of unsaturated hydrocarbons and volatile organic compounds [1]. The atmospheric degradation of aldehydes is primarily controlled by photolysis and reactions with hydroxyl radicals, depending on the molecular structure of the compound. For linear-chain aldehydes such as *n*-butyraldehyde (*n*-butanal), the primary degradation pathway involves reactions with hydroxyl radicals, while reactions with nitrate (NO_3) radicals and ozone (O_3) molecules are comparatively less significant [2].

To investigate the OH-initiated degradation of *n*-butanal, quantum chemical calculations were performed at the M06-2X/6-311++G(d,p) level of theory, which is followed by hydrogen atom abstraction from various C–H bonds. Among the possible abstraction sites, the H-atom abstraction from the carbonyl group (–CHO) is predicted to be the most reactive, with significant activation also observed at the γ-methyl group (C_γ) relative to the carbonyl. The overall rate constant for *n*-butanal degradation is determined as the sum of the rate coefficients for hydrogen abstraction from the primary ($–CH_3$), secondary ($–CH_2–$), and aldehyde (–CHO) groups. The formation of water molecule and related species via the H-abstraction process is both kinetically and thermodynamically favorable. At room temperature and atmospheric pressure, the computed overall rate coefficient is 2.72×10^{-11} cm^3 $molecule^{-1}$ sec^{-1}, which is consistent with available experimental data [3-7].

The atmospheric implications of *n*-butanal have been assessed by estimating key parameters such as its tropospheric lifetime and photochemical ozone creation potential (POCP). Using a global tropospheric daytime average OH-radical concentration of 2×10^6 molecule cm^{-3} (based on a 12-hour average), the calculated atmospheric lifetime is approximately 5.1 hours, indicating its rapid degradation in the atmosphere and potential contribution to photochemical smog formation. The average ozone production resulting from *n*-butanal emissions is estimated to be ~4.2 ppb, with POCP values of 58.2 and 62.5 under typical northwestern European and U.S. urban conditions, respectively.

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