

Low temperature oxidation of butanol: theoretical kinetic modeling

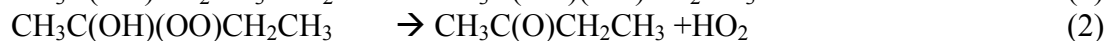
Tatsuo Oguchi,^{1*} Motoki Ito,¹ and Akira Miyoshi²

¹ Toyohashi University of Technology, Toyohashi, Aichi, JAPAN

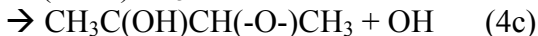
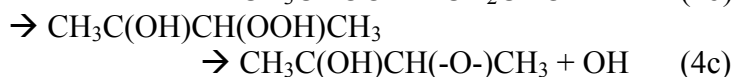
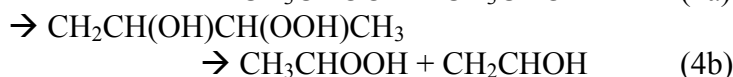
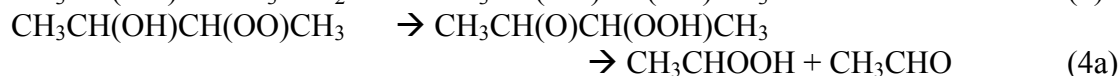
² The University of Tokyo, Bunkyo-ku, Tokyo, JAPAN

* Corresponding author: oguchi@tut.jp

Low temperature oxidation mechanism of 2-butanol was investigated theoretically. The reaction paths for oxidation of some hydroxybutyl radicals formed from 2-butanol were followed by CBS-QB3 level energy calculations as:



and



Other reaction paths were also examined, however, considerable reaction path was not found. Canonical variational TST calculation on the calculated minimum energy path for reaction 1, 3 and multi-well, multi-channel RRKM calculation were performed for the reactions 1-4 to obtain the reaction rate constants. The first formally direct reaction mechanism (the reaction 1 and successive reaction 2) were highly exothermic ($\sim 110 \text{ kJ mol}^{-1}$) and barrierless reaction, so that the rate constant was very large ($1-10 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) even at room temperature and little dependency for pressure and temperature was found. On the other hand, the branching fractions of the reaction 4a-4c and competitive stabilization channel strongly depend on the total pressure and temperature. However, reaction 4a was most important path at any pressure under the 900 K temperature range because indirect reaction 4a was also dominant ($\phi \sim 0.7$) for overall unimolecular reaction of the stabilized peroxy radical. The rate constants obtained in this study were applied for detailed kinetic modeling for auto-ignition of butanols.

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