

Kinetics of Methyl Radical Oxidation at High Pressure

Amit R. Sharma,* Lawrence B. Harding, and Stephen J. Klippenstein

Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

* Corresponding author: asharma@anl.gov

High pressure experimental studies of methyl oxidation with molecular oxygen ($\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O}_2$) show unusual pressure dependences, significantly different from typical falloff curves, at pressures of about 300 bar and temperatures of 300 to 400 K. Similar (unusual) pressure dependence has been observed for the rate coefficient for ozone formation in bath gas, oxidation of chlorine atom with O_2 , chlorine monoxide self-reaction and in some large molecule systems. It has been proposed that the radical-complex mechanism in addition to the usual energy-transfer mechanism contributes to the total rate at such high-pressures. However, no quantitative theoretical estimation of these rates has been published.

At high-pressures, methyl radical or O_2 , or both, form a van der Waals type complex with the bath-gas (R-M, radical-complex). The formation of the radical-bath gas (R-M) complex is related to the strength of the R-M bond in these complexes and at low temperatures and high bath-gas density, many of the radicals could be in the radical-complex state. The R-M radical complex further reacts with the second radical (R) to form a three-body complex. The decomposition of the $\text{CH}_3 \dots \text{O}_2 \dots \text{M}$ complex results in the formation of CH_3O_2 via the $\text{CH}_3 \dots \text{O}_2$ transition state.

In this paper we present a multiple-transition state model and the formal statistical expression for estimating the kinetics of radical- radical-bath gas complex species from first principles. A high-level *ab initio* based potential energy surface is developed for $\text{CH}_3 \dots \text{Ar}$, $\text{CH}_3 \dots \text{He}$, $\text{O}_2 \dots \text{Ar}$, $\text{O}_2 \dots \text{He}$ and $\text{CH}_3 \dots \text{O}_2$ species. The contribution due to the radical-complex mechanism is calculated based on the assumption of a two-transition state model (minimum reactive flux locations) along the reaction path describing formation of the radical-R-M complex and the dissociation of this complex.

We also explore the two-transition state model that does not involve a radical-complex intermediate. In this model the methyl radical reacts with O_2 to form a van der Waals type complex, which is then collisionally stabilized by the bath gas. Assumption of this intermediate complex leads to a two-transition state model, where the outer transition state is configurationally similar to the reactants (termed as “loose”) and the inner transition state occurring near the unimolecular product. The microcanonical and canonical rate is calculated in terms of the sum of states at the two transition states. Comparison is made with experimental data.

Acknowledgement: This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy, under contract number DE-AC02-06CH11357.