

Factorial Analysis of Ethylene Oxide Degradation Process in Tropospheric Chemistry

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1.Introduction

Ethylene Oxide (EtO), one of the volatile organic compounds (VOCs) emitted from the sterilization activities, is known as a carcinogenic substance. In order to achieve the health risk assessment of EtO, understanding of the atmospheric behavior such as emission mechanism and detailed chemical reactions of EtO enables policymakers to control ambient concentration of EtO. The atmospheric lifetime, which is an indicator of the atmospheric stability of air pollutants including EtO, is usually defined by the reactions with OH since OH is a major oxidant in the atmosphere. Because detailed oxidation mechanism of EtO with other oxidants except for OH are unclear, the rate constants of the reaction of EtO with atmospheric oxidants (OH, NO₃, Cl, ClO) were determined by the computational calculations based on the quantum chemistry and transition state theories, and the atmospheric lifetime of EtO was evaluated using the global chemical transport model in this study.

2.Methodology

The optimized structure of EtO, atmospheric oxidants, products of EtO oxidation, and the transition states of oxidation reaction were estimated by Gaussian 16, the quantum chemical calculation software, with the G4//M06-2X/aug-cc-pVTZ level of theory. The rate constants were calculated based on the transition state theory by Gaussian Post Processor (GPOP). The Goddard Earth Observing System Chemistry model (GEOS-Chem v12.9.3) was applied to obtain the distribution of the global concentration of OH, NO₃, Cl, and ClO. The calculated period was from Jan. 2019 to Dec. 2019, and the period Jan. 2018 to Dec. 2018 was treated as the term of spin-off calculations. In terms of emission inventories, CEDS was used for anthropogenic emission and ship emission, GFED was used for biomass burning, and MEGAN was used for BVOC emissions. MERRA2 was used for meteorological inputs. The grid resolution was 2 × 2.5 in latitude × longitude.

3.Results and Discussion

Fig.1 shows the energy diagram of the oxidation reactions of EtO calculated in this study. The results of the computational calculations suggested that the rate constant of the reaction of EtO with OH was calculated to be $3.45 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the rate constant of EtO with Cl was calculated to be $2.13 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which are in good agreement with the experimental values in the previous studies. The rate constant of EtO with NO₃ was calculated to be $5.49 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is about 5 orders of magnitude lower than the rate constant of EtO with OH. The rate constant of EtO with ClO was calculated to be $1.03 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constant of OH addition to EtO was also examined, but the rate constant was calculated to be $2.61 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of which the value was extremely lower than other reactions. The dominant atmospheric lifetime of EtO was 250 days from the loss by OH, and that by Cl follows as 34.3 years. Since the concentration of Cl shows higher than that of OH in marine and coastal areas, the reaction of EtO with Cl should be taken into account in those areas. In other words, EtO was consumed mainly by the reaction with OH in land area and also by the reaction with Cl in marine and coastal areas. Global distributions of the reaction rate of EtO with atmospheric oxidants normalized by the concentration of EtO were evaluated which is shown in Fig.2. The results showed that the rate of EtO decay is particularly high in Japan, China, India, the Middle East, Western Europe, and North America, where the amounts of anthropogenic emission are high. In areas of small anthropogenic emission sources, the loss of EtO was expected to be unprogressive, and EtO will be

either accumulating in the atmosphere or being lost by dry and wet depositions.

4.Acknowledgements

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Keywords: Ethylene Oxide, Quantum chemical calculation, Transition state theory, Tropospheric chemistry, GEOS-Chem

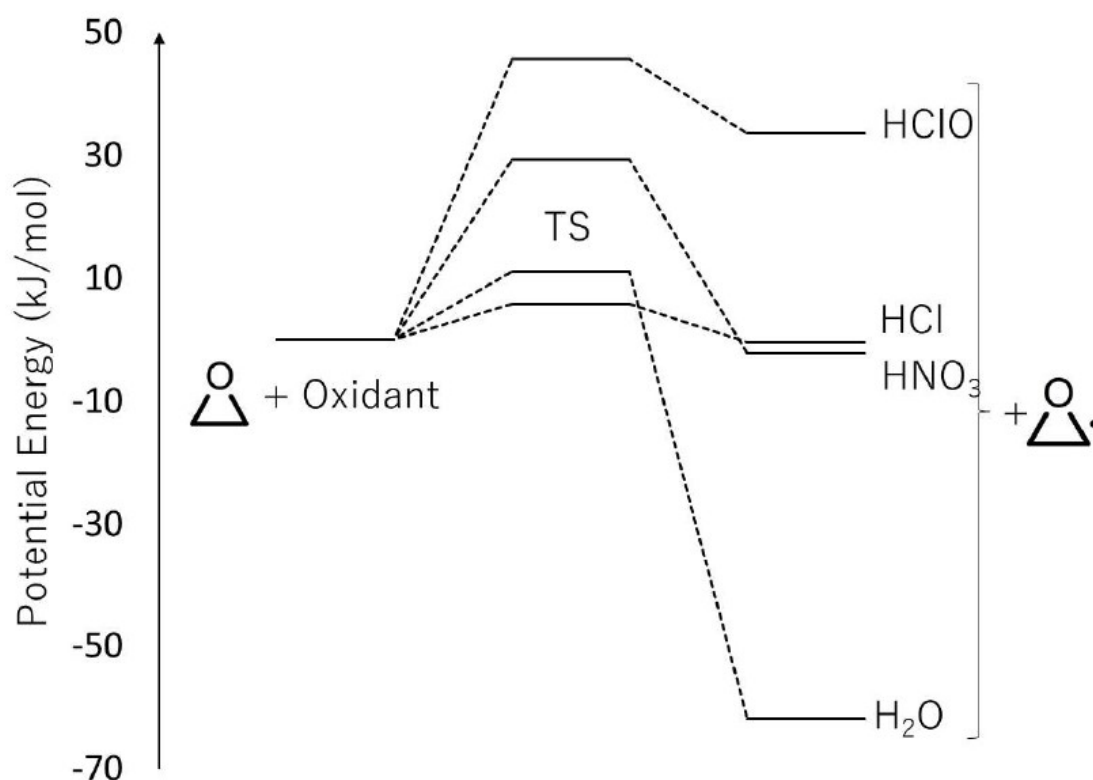


Figure 1 Energy Diagram of the Reaction of Ethylene Oxide

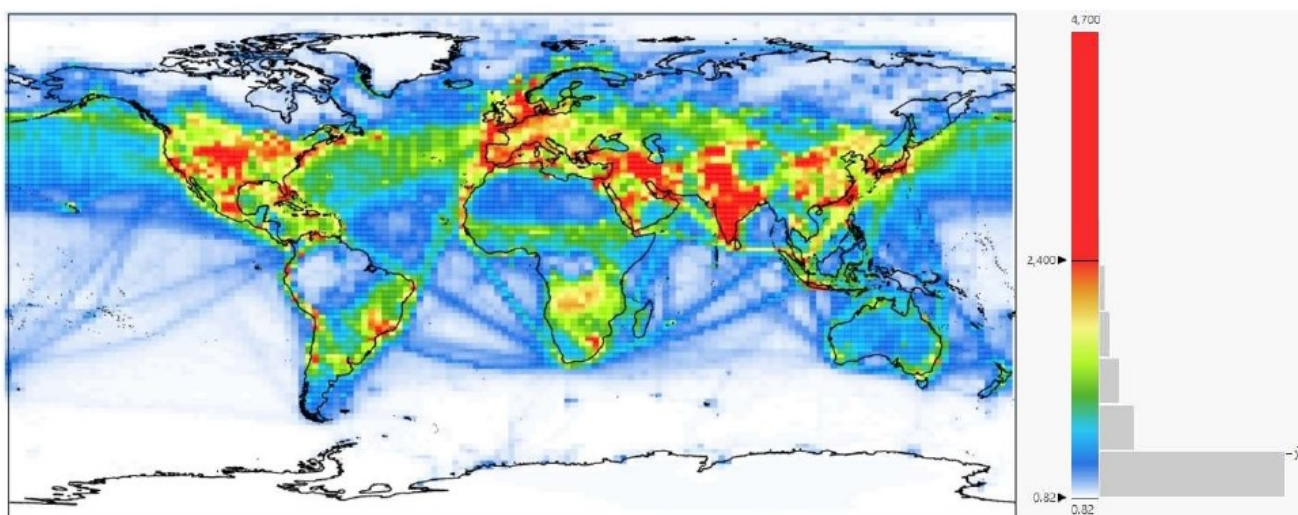


Figure 2 Reaction Rates of Ethylene Oxide with Atmospheric Oxidants Normalized by Ethylene Oxide Concentration