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Formation pathways of HO₂ and OH changing as a function of temperature in photolytically initiated oxidation of dimethyl ether

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Abstract

The time resolved product formation in oxidation of dimethyl ether (DME) has been studied between 298–625 K and 20–90 torr total pressure. Near-infrared frequency modulation spectroscopy (FMS) with Herriott type multi pass optics and UV absorption spectroscopy (UV) were conducted in the same cell. The reaction was initiated by pulsed photolysis in a mixture of Cl₂, O₂, and DME via CH₃OCH₂ radical formation. The reaction process was investigated through FMS measurement of HO₂ and OH, and UV measurement of CH₃OCH₂O₂. The yields of HO₂ and OH are obtained by comparison with reference mixtures, Cl₂, O₂, and CH₃OH for HO₂, and Cl₂, O₂, CH₃OH, and NO for OH, which convert 100% of initial Cl to HO₂ and OH. The CH₃OCH₂O₂ yield is also obtained. It was found that the HO₂ yield increases sharply over 500 K mainly with a longer time constant than that of R + O₂ reaction, while a prompt component exists throughout the temperature range at a few percent yield. OH was found to be produced promptly at a yield considerably larger than that known for the simplest alkanes. The CH₃OCH₂O₂ profile has a prompt rise followed by a gradual decay whose rate is consistent with the slow HO₂ formation. The species profiles were successfully predicted with a model constructed by modifying the existing one to suit the reduced pressure condition. After modification, it was inferred that the HO₂ formation over 500 K is secondary from HCHO + OH and HCO + O₂ and a part of HCO is formed directly from the O₂ adduct, whereas the HO₂ formation below 500 K is governed by CH₃OCH₂O₂ chemistry. The HCO forming pathway via isomerization–decomposition of the O₂ adduct, which was not included in the former models, was supported by our quantum-chemical calculations.

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Keywords: HO₂; Dimethyl ether; Low temperature oxidation; Frequency modulation spectroscopy; Near IR

1. Introduction

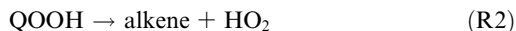
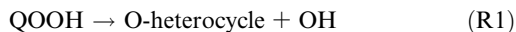
Low temperature oxidation (LTO) of hydrocarbon has drawn attention as it is responsible for autoignition behaviors. A general description

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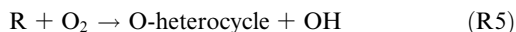
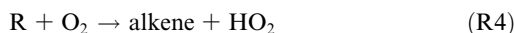
of this reaction mechanism has been established through extensive experimental and theoretical studies [1–3].

In an alkane–oxygen mixture at a moderate temperature (typically 700 K), an alkyl radical formed from the parent alkane undergoes oxygen addition to form an alkylperoxy radical (RO_2). RO_2 may isomerize to a hydroperoxy alkyl radical (QOOH). QOOH has branching pathways of decomposition and second O_2 addition:



(R3) and the following reactions that finally generate two OH dominate at lower temperatures and higher pressures. The OH increment assures the growing chain sequence. As the temperature increases, the dominance shifts from (R1), (R2) and (R3). While (R1) is a chain propagation step, (R2) is a chain termination step forming relatively inactive HO_2 . Consequently, the competition between (R1) and (R3) is an essential determinant of the fuel specific ignition character.

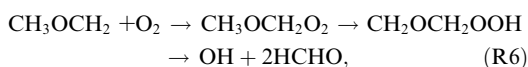
Recently, Taatjes and co-workers derived further insights through time-resolved HO_2 and OH detection in various alkyl + O_2 reactions [4–11]. Their findings include prompt HO_2 and OH formation channels distinguished from slow formation via stabilized RO_2 .



In the most explicated cases of ethane and propane, HO_2 formation is found to be dominant. OH formation is expected to be significant in larger straight alkanes, however, the higher rate of alkyl radical decomposition and the complexity due to radical isomers obscure the detailed analysis of butane and higher alkanes.

Dimethyl ether (DME) is a high cetane number fuel capable of diesel engine combustion. While DME exhibits typical two-stage ignition like *n*-heptane, the simple molecular structure enables detailed chemical mechanistic analysis.

There have been a number of modeling studies of DME oxidation [12–18]. The established model states that DME LTO is a simple form of the above described general mechanism, i.e.:



at reduced pressure where the second O_2 addition is not significant. This mechanism is based on experiments generating CH_3OCH_2 in the presence of oxygen, with analytical techniques like UV

absorption of RO_2 and mass spectroscopy [19–22]. Theoretical investigations of this reaction have also been conducted [23–25]. These studies generally support the dominance of OH formation; however, it does not mean the absence of other pathways such as HO_2 forming ones.

Our recent investigation using the same methodology as developed by Taatjes et al. actually detected HO_2 and OH in a photolytically initiated DME oxidation system [26]. In this study, UV detection of alkyl and alkylperoxy species is additionally conducted in the NIR system in order to further elucidate the complicated reaction mechanism.

2. Experimental section

The experimental setup of frequency modulation spectroscopy (FM) has been described elsewhere [27]. Briefly, the output of a tunable diode laser was two-tone frequency modulated at 600 ± 2.6 MHz and fed into a Herriott type multi-pass cell of 1.5 m cavity length. Only the center region of the probe beam path between the cavity mirrors overlapped the co-axial photolysis beam. HO_2 was detected at 7013.5 cm^{-1} of A–X ($0^+ - 0''$) band and OH was detected by probing a vibrational overtone at 6971.3 cm^{-1} .

The UV absorption optics was constructed in the Herriott setup so as not to harm the NIR multi-pass detectivity. A deuterium lamp (Hamamatsu, L7296-50) was used as a probe light source. The collimated UV light was single-passed through the slits in the Herriott concave mirrors placed for the diode beam passage and detected by a photomultiplier tube (Hamamatsu, R928) after passing through a band-pass filter (Sigma Koki, VPF-25C-10- λ , $\lambda = 228, 253 \text{ nm}$) or a monochromator (Ritsu, MC-25). The signal was averaged 1000 times by a digital oscilloscope. The overlap region between the UV probe and the photolysis beam was estimated to be 40 cm by comparing the HO_2 signals detected with UV and FM. Since the absorption bands of HO_2 and $\text{CH}_3\text{OCH}_2\text{O}_2$ are broadly overlapped [28], the $\text{CH}_3\text{OCH}_2\text{O}_2$ signal was detected at 250 nm and corrected by using FM signal of HO_2 . Peak absorbance was approximately 0.4% at the typical experimental condition. The cross section of $\text{CH}_3\text{OCH}_2\text{O}_2$ was estimated to be $3.57 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 250 nm, which is 1.2 times larger than the previous data [28]. This value reflects the peak yield of $\text{CH}_3\text{OCH}_2\text{O}_2$ modeled in this study. CH_3OCH_2 was also detected at 228 nm with the cross section reported in ref. [29]. The rate constant of CH_3OCH_2 thermal decomposition was separately measured in oxygen-free conditions since the analysis of oxidation products is sensitive to this rate.

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