



Oxidation characteristics and products of five ethers at low temperature



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HIGHLIGHTS

- Characteristics and products of ether oxidations were examined using accelerating rate calorimetry (ARC).
- Three stages of ether oxidation with oxygen were identified.
- Thermal decomposition kinetics were calculated.
- Peroxides of DEE, DIPE, MTBE, and ETBE were quantified by iodimetry analysis.
- The products of the oxidation of five ethers were analyzed and identified.

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ABSTRACT

The oxidation characteristics and products of five ethers – ethyl *tert*-butyl ether (ETBE), methyl *tert*-butyl ether (MTBE), dimethyl ether (DME), diethyl ether (DEE), and diisopropyl ether (DIPE) – were determined using an accelerating rate calorimeter (ARC) at low temperatures. Oxidation temperature and pressure were calculated using temperature–time ($T-t$) and pressure–time ($P-t$) plots, and reaction products were analyzed by gas chromatography–mass spectrometry (GC–MS). Results showed that the oxidation reaction pathway of ethers with oxygen occurred in three stages: (1) promotion of oxygen and peroxide absorption by ether; (2) generation of free radicals by thermal decomposition; and (3) complex oxidation caused by free radicals. Initial auto-oxidation temperatures of DME, DEE, DIPE, MTBE, and ETBE were approximately 393 K, 389 K, 359 K, 413 K, and 383 K, respectively, and the activation energies (E_a) for thermal decomposition were 167.3 kJ/mol, 126.7 kJ/mol, 111.6 kJ/mol, 236.7 kJ/mol, and 159.1 kJ/mol, respectively, for the first-order reaction. Peroxides of DEE, DIPE, MTBE, and ETBE were identified by iodimetry analysis when oxidation temperature was 333 K. Oxidation reaction products were complex and included alcohols, aldehydes, ketones, acids, esters, and carbon dioxide.

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1. Introduction

Dimethyl ether (DME), ethyl *tert*-butyl ether (ETBE), methyl *tert*-butyl ether (MTBE), and other ethers are candidates as “clean fuel” sources because they can improve octane ratings and reduce the emission of carbon monoxide (CO) and unburned hydrocarbons. Ethyl *tert*-butyl ether and MTBE are used in some types of gasoline, added to biomass as an oxygen source [1,2], and used as a fuel [3,4]. In addition, ETBE/ethanol mixtures have attracted attention because they are excellent octane boosters, have high calorific value, generate less NO_x, and promote complete combustion of CO [5,6]. In addition, a mixture of ETBE with ethanol lowers the volatility of ethanol, making it suitable as an additive for

gasoline [7]. The production of ETBE is increasing because ethanol, a component of ETBE, can be produced from renewable biomass [8–11]. Output of MTBE was 5.6×10^6 t/a in 2013 in China [12]. However, the use of fossil fuels can result in serious environmental problems from NO_x, HC, and CO emissions. Consequently, studies have been conducted to develop alternative “clean” fuels. Dimethyl ether (DME) has attracted attention as a substitute for diesel fuel [13–15] because it can be synthesized and possesses good ignition properties. Furthermore, DME produces low emissions and low formation of soot [16–18].

The characteristics of combustion [19,20], oxidation [21], and mechanism of action [22–24] of DME have been reported. Cristina et al. [25] investigated the atmospheric oxidation of methyl and ethyl *tert*-butyl ethers initiated by hydroxyl radicals. The autoxidation of DME with diethyl ether (DEE) and diisopropyl ether (DIPE) has been compared by Naito et al. [26]. The oxidation of MTBE,

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ETBE, diisopropyl ether (DIPE), and *tert*-amyl methyl ether (TAME) was investigated experimentally in a high-pressure jet-stirred reactor (JSR) using high-temperature oxidation [27]. Goldaniga et al. [28] investigated the chemical kinetics of oxidation of MTBE, ETBE, DIPE, and TAME at high temperatures under elevated pressure, both experimentally and computationally, which was used to develop a set of primary oxidation and decomposition reactions for ethers.

Ignition delay times of ETBE/O₂/Ar mixtures were derived from OH radical emissions [29]. Detailed chemical kinetic mechanisms of ethyl methyl, methyl *tert*-butyl, and ethyl *tert*-butyl ethers have been investigated by Yasunaga et al. [30]. Thermal decomposition of ETBE and decomposition catalysis by hydrogen halides [31,32] have been reported at high temperatures. For ETBE reaction kinetics, research has focused on oxidation due to a radical initiator [33–35]. Liu et al. [36] reported flash photolysis resonance fluorescence results for reactions of oxygen O (³P) atoms with aliphatic ethers and diethers in the gas phase. The ETBE oxidation reactions initiated by an OH radical have been reported by Teton et al. [37], Smith et al. [38], Wallington et al. [39]. Zhang et al. [40] reported decomposition pathways of MTBE by theoretical calculation of QCISD(T,E4T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2. Pyrolysis of MTBE was examined by Daly et al. [41], while MTBE oxidation reactions and kinetics initiated by an O or OH radical have been reported by multiple groups [42–45,37,46,39,47,48].

However, data on thermal stability, characteristics, products, and oxidation pathway of ether low-temperature oxidation reactions are not adequate because ethers can come into contact with oxygen during production processes, storage, transportation, and consumption. Ethers react with molecular oxygen at ambient temperatures to form hydroperoxides [26]. Therefore, prolonged exposure in air may induce auto-oxidation to produce explosive organic peroxides during production processes, transportation, and storage of ethers.

The present study describes the reactivity of five ethers with oxygen, the initial auto-oxidation reaction, thermal decomposition and characteristics, oxidation reaction products, and reaction pathways. The results of these studies will be useful for organic synthesis, chemical engineering and processing, and fuel combustion.

2. Materials and methods

2.1. Materials

Dimethyl ether (DME, purity 99.5 wt%) was obtained from Koike Chemical Ind. Ltd., Japan. Methyl *tert*-butyl ether (MBTE, purity 99.0 wt%), DEE (purity 99.0 wt%), and DIPE (purity 99.0 wt%) were obtained from Kanto Chemical Ind. Ltd., Japan. Ethyl *tert*-butyl ether (ETBE, purity 99.0 wt%) was obtained from Sigma–Aldrich Co., Ltd. The O₂ and N₂ gases were obtained from Tomoe Shokai Co., Ltd., Japan.

2.2. Thermal behavior of ether oxidation by ARC

An accelerating rate calorimeter (ARC) (Arthur D. Little Inc. USA, ARC2000) was used to evaluate the safety of hazardous chemicals and energy materials [49–51]. An ARC apparatus is sensitive enough to follow a self-heating rate adiabatically, closely simulating conditions in an actual reservoir [52,53]. Therefore, it can be used to track and study the ether oxidation process.

A sample of 0.3–0.5 g of an ether (such as ETBE) was introduced into a high-pressure vessel (ARC bomb, bomb material was HastelloyC) using a syringe. To understand the characteristics of oxidation and the order of the thermal decomposition reaction, the effects of heating and pressure on ether oxidation were

investigated under atmospheres of oxygen and nitrogen at an initial pressure of 1.0 MPa (DME: 2.0 MPa).

To observe oxygen absorption, the exothermic processes, and characteristics of the oxidation reaction, an ARC mode of “heat-wait-search” (HWS) was used. Working conditions for the isothermal tests were: a starting temperature of 323 K; an ending temperature of 473–523 K; a temperature step of 5 K; a slope sensitivity of 0.02 K/min; a wait time of 20 min; and a search time of 10 min.

2.3. Oxidation product analysis by GC–MS

The oxidation products were analyzed by gas chromatography–mass spectrometry (GC–MS). Both gaseous and liquid ether oxidation products were formed. After completion of the reaction, to collect gaseous products, the temperature was lowered to room temperature, and gases were collected using a special gas collection bag. The liquid products remained in the reaction bomb. Both the gases and liquids were analyzed by GC–MS using a GCMS-QP5000 (Shimadzu Corp., Japan.) with an electron impact ionization detector (70 eV), equipped with a DB-WAX fused silica capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm; J&W Scientific Inc.).

The GC–MS analysis conditions were:

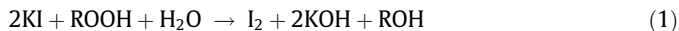
- *Gas analysis conditions:* Column temperature was held at 313 K for 1 min, and then increased to 423 K at a rate of 4 K/min. The carrier gas was helium with a flow rate of 1.0 mL/min, pressure of 49 kPa, and a split ratio of 200:1. Scan time and mass range were 1 s and 30–300 *m/z*, respectively. Detector and injector temperatures were 548 K and 523 K, respectively.
- *Liquid analysis conditions:* Column temperature was held at 323 K for 1 min and then increased to 473 K at a rate of 5 K/min. The carrier gas was helium with a flow rate of 1.2 mL/min, pressure of 47 kPa, and a split ratio of 70:1. Scan time and mass range were 1 s and 30–500 *m/z*, respectively. Detector and injector temperatures were 548 K and 523 K, respectively.

2.4. Ether oxidation at low temperatures

A 5-g sample of ether was introduced into a 500-mL high-pressure reaction kettle under an atmosphere of oxygen at an initial pressure of 0.5 MPa. Then, the sample was heated to 330 K under stirring, where ether oxidation occurred, followed by peroxide analysis every 2 h.

2.5. Peroxide analysis by iodimetry

Peroxide concentration was measured using iodimetry [26,54]. For this test, a quantity of sample dissolved in toluene was added to aqueous potassium iodide, which reduced the peroxides present (Eq. (1)). An equivalent amount of iodine was liberated, which was titrated with sodium thiosulfate solution (Eq. (2)). Results were quantified as milligrams per kilogram (ppm) of peroxide:



3. Results and discussion

3.1. Behavior of temperature and pressure during the oxidation reaction process

To study the oxidation reaction process of the five ethers, pressure and temperature over time were measured using ARC. For comparison, heating experiments also were conducted under

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