

A comparative study on the autoxidation of dimethyl ether (DME) comparison with diethyl ether (DEE) and diisopropyl ether (DIPE)

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Abstract

The Japanese government is planning to introduce DME as a substituted energy for oil and LNG. Introduction of DME could contribute greatly to both the prevention of global warming and the formation of resource-recycling societies. In these circumstances, a safety assessment of DME is very important when DME is used on a large scale. There is a possibility that prolonged exposure in air induces autoxidation to produce explosive organic peroxides during transportation and storage of DME. Therefore, the reactivity of DME with oxygen and the mechanism of the autoxidation were investigated. Accelerating Rate Calorimetry (ARC) was used to evaluate the thermal stability of DME and DIPE, a known peroxide producers, under adiabatic and various atmospheric conditions. In ARC studies of DME under oxygen, exothermic decompositions were detected although its self-heating rate was low in comparison with DIPE. Oven storage tests were carried out and iodimetry was used to measure the concentration of peroxides produced from DME in comparison with DIPE and DEE. However, no products could be found for DME either by GC/MS or by iodimetry, while some evidence of autoxidation of both DEE and DIPE were obtained from these experiments.

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1. Introduction

In recent years, there has been increasing scientific evidence to suggest that the use of fossil fuels leads to serious environmental problems (NO_x, SO_x emissions, etc.). Considerable research has thus been carried out into alternative ‘clean’ energy sources. In the last few years, attention has been increasingly focused on the use of dimethyl ether (DME) as a substitute diesel fuel. DME is a synthetic fuel with good ignition properties, low emissions and low soot formation. DME also can be manufactured at a competitive price from natural gas-derived methanol and a variety of other natural resources. Such features could contribute greatly to both the prevention of global warming and to the formation of resource-recycling societies.

DME has similar physical properties to liquid petroleum gas (LPG) thus it is predicted that existing LPG technology could be used when DME is introduced into the energy system. Japan currently produces DME at a rate of 10,000 t/year for use as an environmentally benign aerosol propellant but by 2006 the Japanese government has a plan to introduce DME as a fuel for power generation so over 170,000 t will be imported annually. DME caused several accidents in the past. A feasibility study including an assessment of the reactivity, ignition and explosion characteristics, and risks to both human health and the environment needs to be carried out before such a large-scale introduction can occur (David, 1980). It is well known that ethers react with molecular oxygen at ambient temperatures to form hydroperoxides (Urban, 1995). There is a possibility that prolonged exposure in air induces autoxidation to produce explosive organic peroxides during transportation and storage of DME.

The aim of this study was to investigate the reactivity of DME with oxygen and assess safety in comparison with DIPE and DEE which are well known as peroxide producers.

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2. Experimental

In order to investigate the reactivity of DME to undergo autoxidation in air, experiments were carried out at both accelerated and fixed conditions under a closed system.

2.1. Samples

Dimethyl ether (99.9%), diethyl ether (99.5%) and diisopropyl ether (99.7%) were obtained from Mitsubishi Gas Chemical Co., Inc., Kanto Kagaku, and Nippon Petrochemical Co., Ltd, respectively. All chemicals were used without further stabilizer.

2.2. Autoxidation at accelerated conditions

The experiments were carried out using an Accelerating Rate Calorimeter (ARC), which was distributed by Arthur D. Little, Inc. and modified for gas introduction (Richard & Dahn, 1999). Five grams of samples are introduced into small high-pressure vessels (ARC bombs) called HastelloyC. ARC test had been carried out with stainless steel, titanium, and HastelloyC, but there were no significant effects observed from materials so HastelloyC that contained few Fe was used. The samples in the ARC bombs were pressurized by dried air (1 MPa). The working conditions were set up as follows: (1) The bomb temperature, which started at 313 K, was increased by increments of 10 K to a final temperature of 423 K. Each step of the procedure was followed by a waiting period of 240 min. (2) The other was that the bomb temperature, which started at 303 K, was increased by increments of 3 K to a final temperature of 433 K. Each step of the procedure was followed by a waiting period of 20 min. More detailed behavior of pressure at each temperature can be observed from the former.

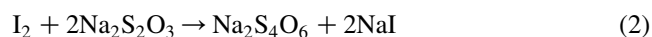
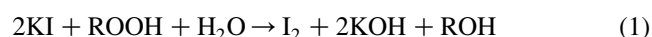
In order to investigate the reactivity of DME in comparison with DEE and DIPE, isothermal tests were carried out for DME, DEE and DIPE. The working condition is shown in Table 1.

2.3. Autoxidation at fixed conditions

2.3.1. Measurement of peroxides production

Samples of DME, DEE, and DIPE (2 g) were introduced into ARC bombs and sealed via a stop valve (Swagelok SS-43TS4). Dried air from gas cylinder (1 MPa) was applied

and the ARC bombs were stored isothermally at 313, 333, and 353 K in a constant temperature oven DK400T (Yamato Science Co., Ltd). At determined storage times the samples were pumped in 250 ml flask. In case of DME, the gas was liquefied by dry ice and pumped in vacuum vessel. Then it was put in 250 ml flask. Concentration of peroxide was measured by iodimetry according to JPI (the Japan Petroleum Inst.) standard 5S-46-96. In this test, a quantity of sample dissolved in toluene is contacted with aqueous potassium iodide solution and the peroxides present are reduced by the potassium iodide (Eq. (1)). An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution (Eq. (2)). The results are calculated as milligrams per kilogram (ppm) of peroxide.



2.3.2. Measurement of oxygen consumption

The decrease of oxygen indicates the degree of autoxidation. Therefore oxygen consumption was measured after the isothermal test. The same samples as prepared for Section 2.3.1 were stored in a constant temperature bath at 373 K. After the storage test, the sample gas in the ARC bomb was analyzed by gas chromatograph (GC8A, Shimadzu Corp.). Oxygen concentration was determined in comparison with nitrogen concentration.

2.4. Autoxidation under various pressurized atmospheres

In order to investigate the effect of initial concentration of oxygen, the ARC study was carried out under various pressurized atmospheres; air, 50% oxygen and 50% nitrogen, and 100% oxygen. The working conditions of DME are shown in Table 2. A detailed description of the adiabatic tests can be found in Section 2.2.

After the ARC tests, product determination was carried out by gas chromatography-mass spectrometer (GC/MS-QP5000, Shimadzu Corp.).

Table 1
Working condition for the Isothermally tests of ARC

Bomb material	HastelloyC
Start temperature	313 K
End temperature	423 K
Slop sensitivity	0.02 K/min
Heat step	10 K
Wait time	240 min
Sample mass	Approximately 5 g
Pressurized atmospheres	Air

Table 2
Working condition for the adiabatic tests of ARC

Bomb material	HastelloyC
Start temperature	303 K
End temperature	433 K
Slop sensitivity	0.02 K/min
Heat step	3 K
Wait time	0 min
Sample mass	Approximately 5 g
Pressurized atmospheres	Air, O ₂ 50%, O ₂ 100%

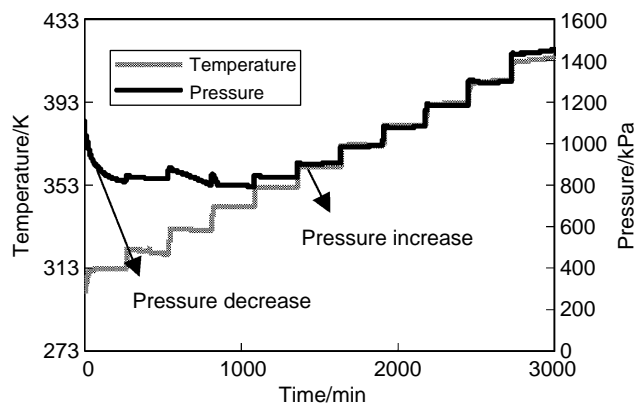


Fig. 1. Temperature and pressure vs. time profile for isothermally tests of DIPE.

3. Results and discussion

3.1. Autoxidation at accelerated conditions

The temperature and pressure vs. time profile for isothermal tests of DIPE, DEE, and DME are shown in Figs. 1–3, respectively. A pressure decrease can be seen in the profile for DIPE at approximately 313 K. A pressure increase was detected at approximately 363 K. No exothermal reaction was detected in this profile.

In the case of DEE, a pressure decrease can be seen at approximately 353 K. A pressure increase was detected at approximately 363 K. No exothermal reaction was detected in this profile.

In case of DME, a pressure decrease can be seen at approximately 373 K. A pressure increase was detected at approximately 383 K. No exothermal reaction was detected in this profile.

It is thought that a pressure decrease corresponds to the uptake of oxygen by the ether, the start of the autoxidation chain reaction, and a pressure increase corresponds to simultaneous decomposition of the produced peroxides. This result shows that the autoxidation onset temperature of

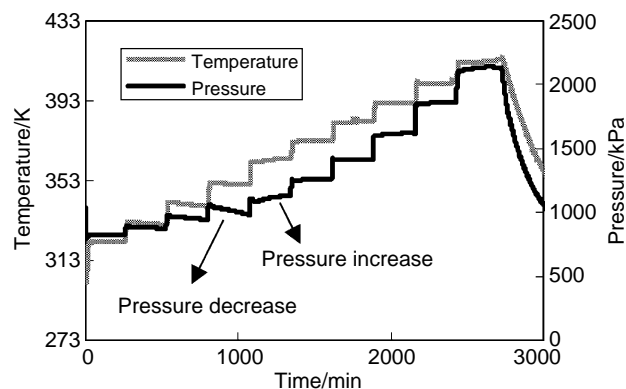


Fig. 2. Temperature and pressure vs. time profile for isothermally tests of DEE.

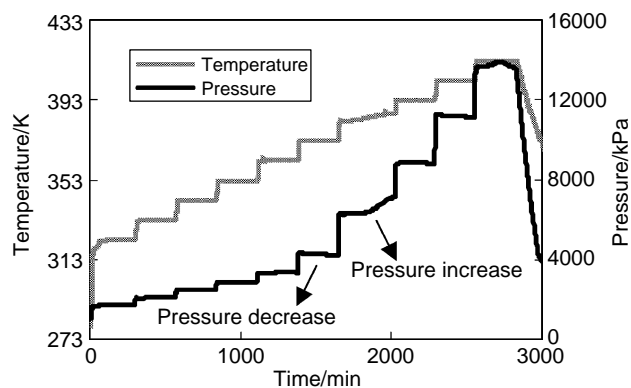


Fig. 3. Temperature and pressure vs. time profile for isothermally tests of DME.

DME reaction is high in comparison with DIPE and DEE. This means DME autoxidation is harder to occur relative to DIPE and DEE, although small exothermal reactions are occurring.

3.2. Autoxidation at fixed conditions

3.2.1. Measurement of peroxides production

The variation of peroxide concentration with storage time for samples of DIPE, DEE and DME at 313, 333, and 353 K are shown in Figs. 4–6, respectively.

The data show that at 313 K [ROOH] vs. storage time profiles for DIPE and DEE are similar, whereas peroxides within the range detectable by iodimetry were not detected from DME.

At 333 K, the maximum [ROOH] produced from DIPE autoxidation (2161 ppm) was higher than that produced from DEE autoxidation (1609 ppm). DIPE reached a maximum [ROOH] after only 24 h of storage. DEE reached a maximum [ROOH] after 120 h of storage. Fig. 5 shows that rate of DIPE autoxidation is faster than that of DEE

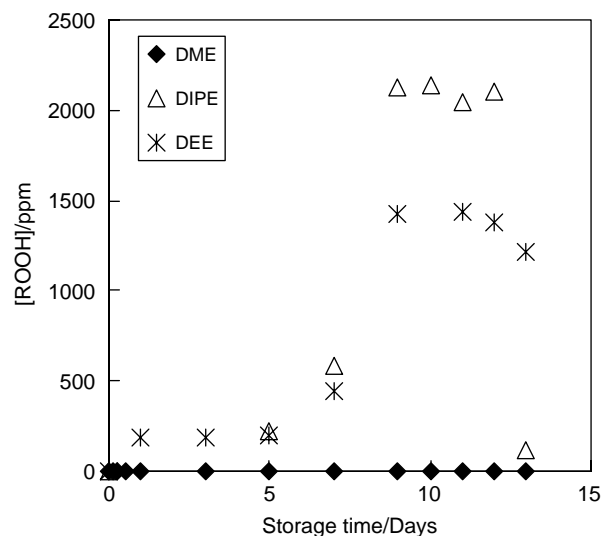


Fig. 4. [ROOH] vs. storage time for DIPE, DEE and DME stored at 313 K.

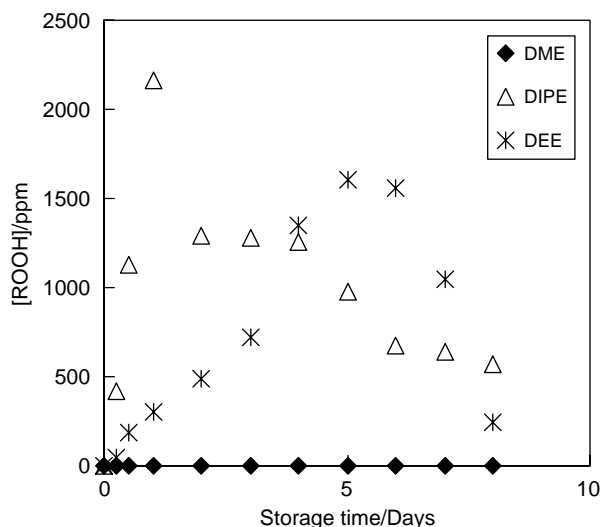


Fig. 5. [ROOH] vs. storage time for DIPE, DEE and DME stored at 333 K.

at 333 K. Peroxides within the range detectable by iodimetry were not detected from DME.

At 353 K, the maximum [ROOH] produced from DEE (3196 ppm) was much higher than that produced from DIPE autoxidation (776 ppm). Both DEE and DIPE reached a maximum [ROOH] after only 24 h of storage. All peroxides had decomposed after 72 h of storage. Fig. 6 shows that the rate of autoxidation of DIPE has been reported to be faster than that of DEE thus it is thought that the peroxides produced decompose very quickly at higher temperature regions. Peroxides within the range detectable by iodimetry were not detected from DME.

3.2.2. Measurement of oxygen concentration

Oxygen concentration vs. storage time profile is shown in Fig. 7. Oxygen in the ARC bombs of DIPE and DEE was decreased after 2 h. Only 3% oxygen was remained in

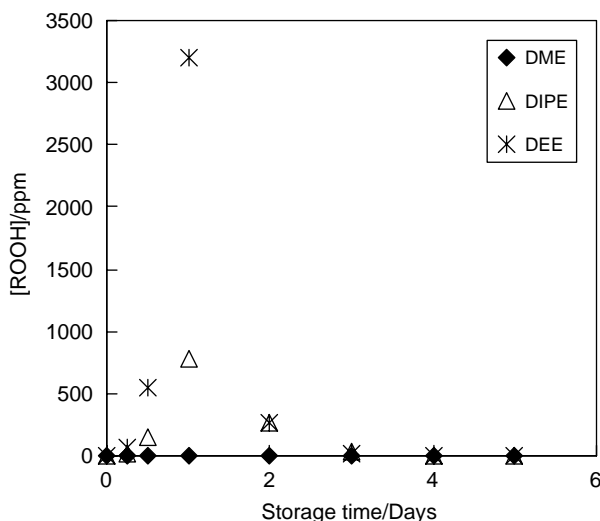


Fig. 6. [ROOH] vs. storage time for DIPE, DEE and DME stored at 353 K.

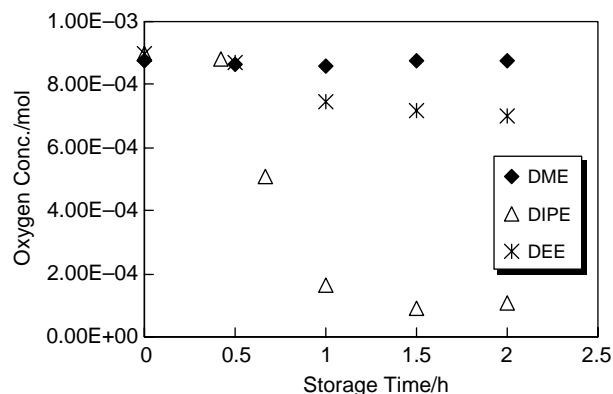


Fig. 7. Oxygen conc. vs. storage time for DIPE, DEE and DME stored at 373 K.

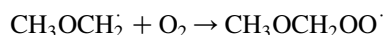
the DIPE bomb. On the other hand, oxygen in the DME bomb was not changed.

This result indicated that the reactivity of DIPE and DEE is higher than that of DME.

3.3. Autoxidation under various pressurized atmospheres

The pressure vs. temperature profiles for the adiabatic test under various pressurized atmospheres of DME are shown in Fig. 8.

The pressure change with temperature under 100% oxygen condition is rather low in comparison with under 50% oxygen. And they are noticeably low in comparison with under air. Oxygen in air (20% oxygen) should not be enough to promote the autoxidation. The result indicated that following scheme—DME oxidation (Curran, Fischer, & Dreyer, 2000; Nelson et al., 1990)—was promoted by 50 and 100% oxygen conditions.



Carbon dioxide and carbon monoxide which are the decomposition products were identified by GC/MS after the adiabatic tests of ARC.

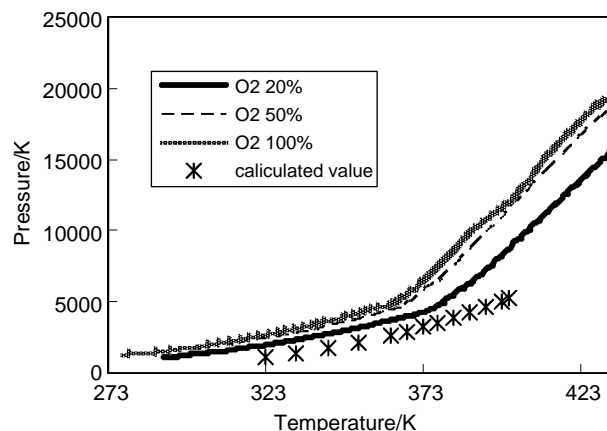


Fig. 8. Pressure vs. temperature profiles for DME under various pressurized atmospheres.

This result suggested that there is a possibility of DME autoxidation under oxygen rich conditions though it is low in comparison with DIPE and DEE.

4. Conclusion

In this study, ARC and oven storage tests were used to investigate the reactivity of DME with oxygen and assess the safety of DME.

ARC studies showed initial temperatures of pressure decrease and increase were 373 and 383 K in isothermal ARC condition of DME. They are higher than those of DEE and DIPE. This means DME autoxidation is harder to occur in comparison with DEE and DIPE. Oven storage tests showed that [ROOH] produced from DME autoxidation at 313, 333 and 353 K were below the range detectable by iodimetry (100 ppm). In addition, both the oxygen decrease rate of DME and the reactivity of DME at 373 K are low. Under these conditions the rate of DME autoxidation is considerably lower than that of DEE and DIPE. ARC studies under various pressurized atmospheres showed initial oxygen concentration had an effect on the temperature of initiation. Decomposition product studies

after ARC adiabatic tests showed carbon dioxide and carbon monoxide. It is concluded that although DME has the capability to undergo autoxidation under oxygen rich conditions, the rate of autoxidation is small relative to DIPE and DEE.

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