

# Influence of dimethyl sulfoxide on exothermic decomposition of peroxide-containing tetrahydrofuran

Noriko Ooizumi<sup>\*†</sup>, Satoru Yoshino<sup>\*</sup>, Mieko Kumasaki<sup>\*</sup>, and Atsumi Miyake<sup>\*</sup>

<sup>\*</sup>Graduate School of Environment and Information Sciences  
Yokohama National University,  
79-7 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, JAPAN  
TEL : +81-45-339-3981 FAX : +81-45-339-4011

<sup>†</sup>Corresponding address : d10HF003@ynu.ac.jp

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## Abstract

Tetrahydrofuran (THF), which is known for being susceptible to autoxidation, is often used with dimethyl sulfoxide (DMSO) as mixture solvent. In this study, we investigated the influence of DMSO on the exothermic decomposition of peroxide containing THF, which may lead to an accidental explosion. THF was pressurized by oxygen and kept at a fixed temperature to produce peroxide. Spectroscopic analysis and iodometric titration showed that THF sample contains various peroxides and decomposition products. Thermal analysis with differential scanning calorimetry (DSC) revealed that the time to exothermic decomposition of THF peroxide is shortened in the presence of DMSO. The activation energy, which was calculated on the assumption that the mechanism of the reaction does not vary depending on temperature, was found to decrease by mixing with DMSO. This result agrees with the fact that the time to exothermic decomposition of peroxide is shortened in the presence of DMSO.

**Keywords** : peroxide, mixing hazard, tetrahydrofuran, dimethylsulfoxide, exothermal decomposition

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## 1. Introduction

Organic solvents are widely used in chemical processes and often used in mixed solvent systems. If a reactive substance such as a peroxide is produced unexpectedly during the use of organic solvents, it may cause a runaway reaction and lead to an accident. Peroxides have caused some serious accidents by explosions<sup>1)</sup>. Therefore, it is necessary to clarify the mixing hazards of peroxides and solvents, in order to prevent accidents and use organic solvents more safely. Tetrahydrofuran (THF), which is known for being susceptible to autoxidation<sup>2), 3)</sup>, is often used with dimethyl sulfoxide (DMSO) as mixture solvent. In this study, we investigated the influence of DMSO on the exothermic decomposition of peroxide containing THF, which may lead to an accidental explosion. THF was pressurized by oxygen and kept at a fixed temperature to produce peroxides. Spectrometry and iodometric titration was used to composition analysis of THF sample. Thermal

analysis was performed to reveal the thermal behavior of exothermic decomposition of THF peroxide in the presence of DMSO.

## 2. Experimental

### 2.1 Materials

Figure 1 and Table 1 show the chemical formula and physical properties of materials used in this study.

### 2.2 Production of peroxide-containing THF

THF (4 mL) was pressurized with oxygen to 0.99 MPa in a SUS316 closed vessel (total volume 8 ml, Fauske & Associates), and held at 40 °C for 55 days. It has been reported that 0.99 MPa oxygen was consumed by THF in seven days at 40 °C<sup>4)</sup>. We repeated the pressurization with oxygen every five days. This sample will be referred to as the THF-AH40 (THF After Holding at 40 °C) in this report.

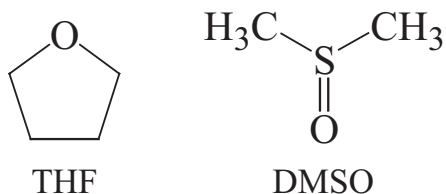


Fig. 1 Chemical formula of materials.

Table 1 Physical properties of materials.

	THF	DMSO
CAS-No.	109-99-9	67-68-5
Concentration [%]	99.5	99.9
Manufacturer	Wako Pure Chemical Industries	Wako Pure Chemical Industries
b.p. [°C]	65	189
m.p. [°C]	-108.5	18.5
Steam pressure [kPa]	19.3	0.06
Dipole moment[D]	1.7	4.6

### 2.3 Spectroscopic analysis

The infrared spectra of THF-AH40 were recorded by infrared spectroscopy on a FT-IR 420 (JASCO) to measure the composition of THF-AH40.

### 2.4 Iodometric titration

The peroxide concentration of THF-AH40 was measured by iodometric titration. After the addition of appropriate amounts of 99.9 % 2-propanol, 99.7 % acetic acid and potassium iodide powder to the sampled materials under reflux, the liquid was titrated with 0.01 mol L<sup>-1</sup> aqueous solution of sodium thiosulfate. The reagents for this titration experiment were provided by Wako Pure Chemical Industry.

### 2.5 Thermal analysis

Differential scanning calorimetry Q-200 (TA-instruments) was used to compare the thermal behavior of THF-AH40 to THF-AH40/DMSO. THF-AH40 and DMSO were mixed at a 1 : 1 volume ratio. The samples were put into the SUS303 stainless closed crucible. After heating to the desired temperature at a rate of 10 K min<sup>-1</sup>, the samples were held at isothermal temperature. It has been reported that the onset temperature of the exothermic peak of THF peroxide is around 110 °C<sup>5)</sup>. The isothermal temperatures were 110, 105, 100, 95, and 90 °C. When the Heat Flow decreased and became constant, we regarded it as the end of the reaction and stopped each isothermal differential scanning calorimetry (DSC) experiment. After the isothermal DSC experiment, the heating DSC experiment was performed. If there was no exothermic peak around 110 °C, the thermal decomposition of THF peroxide was deemed to have finished.

## 3. Results and discussion

### 3.1 Composition analysis of peroxide-containing THF

Figure 2 shows the FT-IR spectra of THF and THF-AH40. The peaks of THF-AH40 were identified as the OO-H

peroxide stretch at 3330 cm<sup>-1</sup>, the C=O carboxylic acid stretch at 1720 cm<sup>-1</sup> and the C=O lactone stretch at 1765 cm<sup>-1</sup>. The peaks at 1423 cm<sup>-1</sup> and 1319 cm<sup>-1</sup> are also characteristic of an O-H carboxylic acid stretch. It has been reported that carboxylic acid and lactone are products of the decomposition of peroxide<sup>6), 7)</sup>. Previous studies showed that a hydroperoxide is formed at an early stage in the autoxidation of THF. It has also been reported that  $\gamma$ -butyrolactone (GBL) is formed by hydroperoxide and that GBL decomposes into  $\gamma$ -hydroxybutyric acid and succinic acid<sup>2), 8)</sup>.

Because the presence of peroxide was indicated by FT-IR, iodometric titration was performed to calculate the concentration. Iodometric titration is a method to determine the concentration of iodine liberated from hydroperoxide. However, it has been reported that correlativity between peroxide concentration by iodometric titration and the heat of reaction by DSC examination was lost in the case of THF pressurized with oxygen and held at 40 °C long term<sup>2)</sup>. In addition, it has been reported that hydroperoxide produces dialkylperoxide by a bimolecular reaction<sup>2)</sup>. Figure 3 shows this change in the structure of the peroxide. According to the iodometric titration, the concentration of peroxide was 5.9 mol%. There is a possibility that the calculated concentration of peroxide was lower than the real concentration, but at least 5.9 mol% of hydroperoxide is present. Therefore, THF-AH40 contained 5.9 mol% of hydroperoxide and was presumed to contain peroxides with different structures and decomposition products.

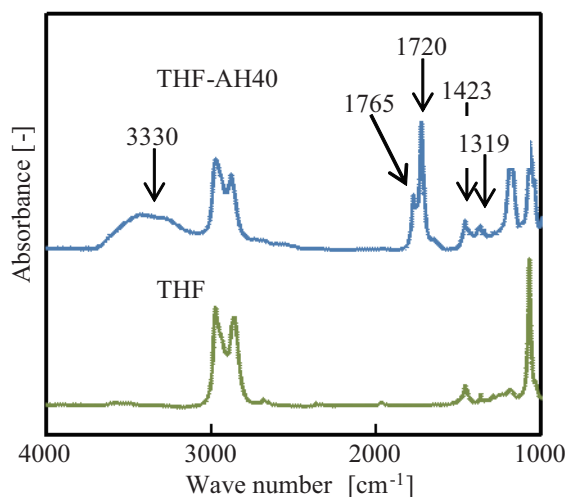


Fig. 2 Spectral peaks of THF-AH40 and THF.

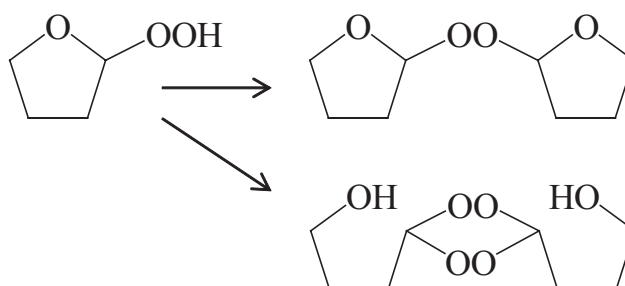


Fig. 3 Reaction of hydroperoxide to dialkylperoxide<sup>2)</sup>.

### 3.2 Thermal analysis

Figures 4 and 5 show DSC curves of THF-AH40 and of THF-AH40/DMSO, respectively, at each temperature.

The slope of the curve of the exothermic peak becomes steep as the experimental temperature increases. The heat release rate also tends to increase as the experimental temperature increases. There seem to be several exothermic peaks in the curves for THF-AH40. Several exothermic peaks also appear prominently in the curves for THF-AH40/DMSO. By spectroscopic analysis, THF-AH40 was considered to contain various peroxides. Therefore, it is suggested that the presence of multiple exothermic peaks depends on these various peroxides which differ in reactivity in DMSO.

### 3.3 Kinetic analysis

In this study, on the assumption that decomposition of the THF peroxide contributes to exothermic behavior, the thermal conversion rate  $u$  was calculated instead of the reaction rate  $C$ . The following equation shows how the thermal conversion rate  $u$  is calculated.

$$u(t) = \frac{\int_0^t q(t) dt}{\int_0^\infty q(t) dt}$$

$$C \approx u$$

In this equation,  $q$  is heat release rate and  $t$  is reaction time. Figure 6 and 7 show the reaction times of thermal decomposition of THF-AH40 and THF-AH40/DMSO, respectively. Table 2 compares the times that THF-AH40 and THF-AH40/DMSO take to reach a thermal conversion rate of 0.8 ( $u = 0.8$ ).

On the whole, the reaction time of THF-AH40/DMSO was shorter than that of THF-AH40. THF-AH40/DMSO reaches  $u = 0.8$  more than twice as fast as THF-AH40, at all experiment temperatures, clearly showing that the time to exothermic decomposition of peroxide is shortened in the presence of DMSO.

On the assumption that the mechanism of the reaction does not vary depending on temperature, the following equation can be written about the thermal conversion ratio<sup>9)</sup>:

$$\frac{q_2}{q_1} = \frac{t_1}{t_2} = \exp\left\{\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\}$$

$$\ln\left(\frac{1}{t}\right) + \frac{AE}{RT} = const.$$

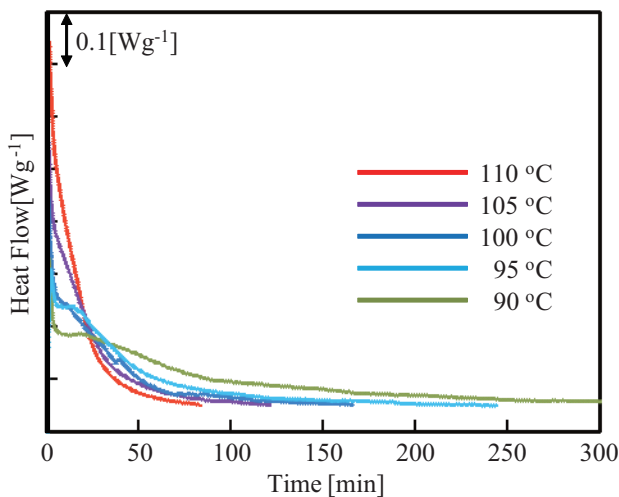


Fig. 4 Isothermal DSC curves of THF-AH40.

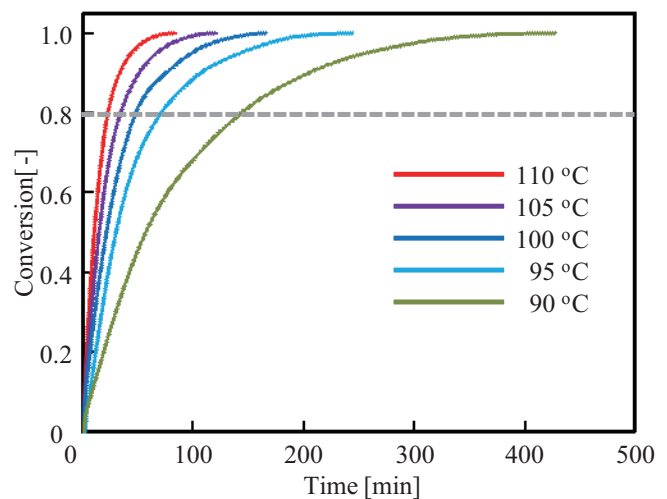


Fig. 6 Thermal conversion rate of THF-AH40.

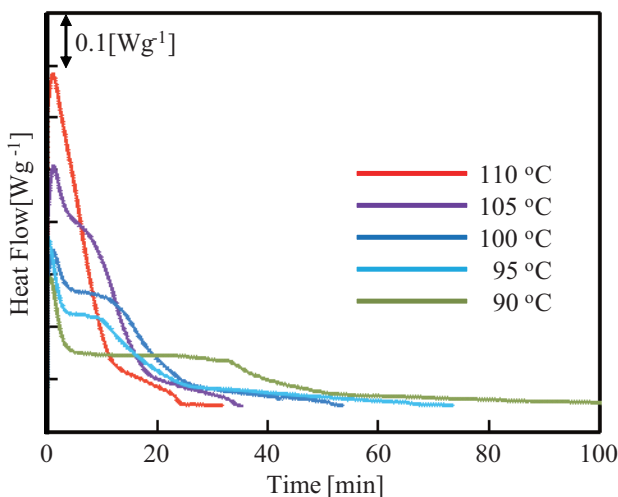


Fig. 5 Isothermal DSC curves of THF-AH40/DMSO.

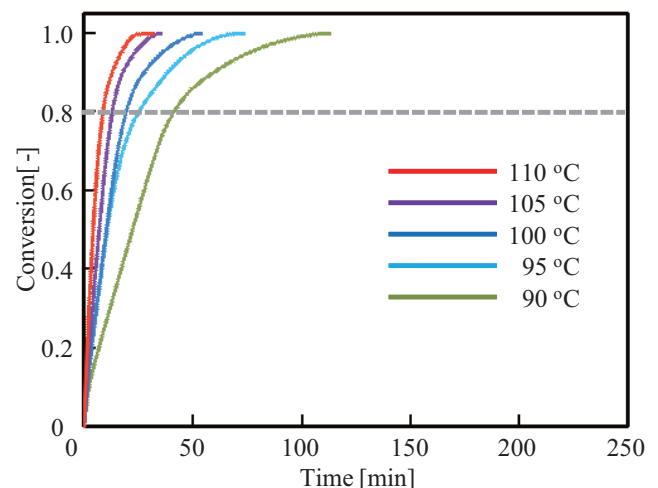
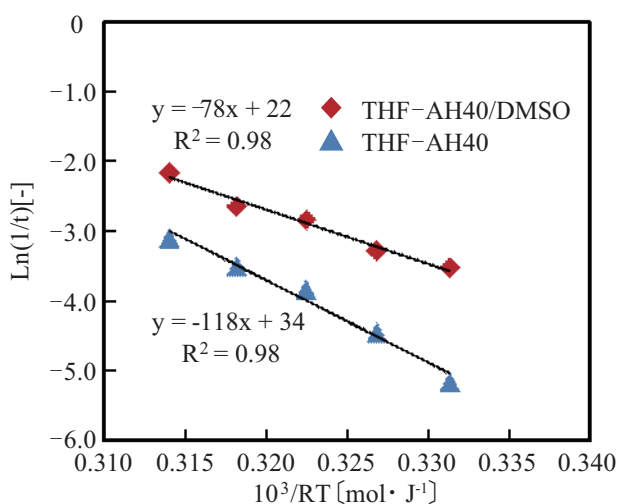


Fig. 7 Thermal conversion rate of THF-AH40/DMSO.

**Table 2** Comparison of time (min) to reach thermal conversion rate  $u = 0.8$ .

$u = 0.8$		
Isothermal Temperature [°C]	THF-AH40	THF-AH40/DMSO
90	174	33.9
95	71.0	26.5
100	46.1	17.0
105	32.9	14.0
110	22.0	8.6

**Fig. 8** Arrhenius plot for determining activation energy ( $u = 0.8$ ).

This equation can provide an activation energy  $E$  from a plot of the reciprocal of the reaction time  $t$  against the reciprocal of the experiment temperature  $T$  and gas constant  $R$ . Figure 8 shows the Arrhenius plot at thermal conversion rates of  $u = 0.8$ .

The linear plots were obtained with  $R^2$  values of 0.98 at  $u = 0.8$ . A similar linearity was seen in other thermal conversion rates as well. The average value of activation energy of THF-AH40 for  $u = 0.1$  to 0.9 is  $108 \text{ kJ mol}^{-1}$  and that for THF-AH40/DMSO is  $79 \text{ kJ} \cdot \text{mol}^{-1}$ . This decrease in activation energy by mixing with DMSO indicates that the reactivity of THF peroxide increases in the presence of DMSO.

DMSO produces sulfone and dimethyl sulfide (DMS) by thermal decomposition<sup>10,11</sup>. To synthesize DMSO, an organic peroxide is used in the oxidation of DMS to DMSO<sup>12</sup>. It has been reported that DMS can decompose peroxide<sup>13</sup>. A previous study showed that in the presence

of acids, hydroperoxides could react with DMS and that decomposition of hydroperoxides was catalyzed by acid (such as carboxylic acids)<sup>14</sup>. The FT-IR spectra suggested the existence of the carboxylic acid of THF-AH40. Therefore, in this study, it is suggested that DMS, which was produced by thermal decomposition of DMSO, may react with THF peroxide and promote the decomposition of THF peroxide.

## 4. Conclusions

The influence of DMSO on the exothermic decomposition of peroxide contained in THF was experimentally investigated by thermal analysis. The following conclusions were derived:

- 1) THF, which was pressurized with oxygen and held at  $40^\circ\text{C}$  for 55 days, contains various peroxides and decomposition products.
- 2) The time to exothermic decomposition of THF peroxide is shortened in the presence of DMSO.
- 3) The decrease in activation energy by mixing with DMSO agrees with the fact that the time to exothermic decomposition of peroxide is shortened in the presence of DMSO.

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## 過酸化物を含有するTHFの発熱分解におけるDMSOの影響

大泉範子\*†, 吉野悟\*, 熊崎美枝子\*, 三宅淳巳\*

テトラヒドロフラン(THF)は自動酸化されやすい溶媒として知られている。またTHFは極性溶媒のジメチルスルホキシド(DMSO)との混合溶媒としてよく用いられる。本研究ではTHFとDMSOの混合系を対象とし、過酸化物を含有するTHFの発熱分解に及ぼすDMSOの影響を実験的に調査した。

THF試料として、THFに酸素を加圧して等温保持し、自動酸化をうながすことでTHF過酸化物を生成させた。この試料の組成を把握するため分光分析およびヨウ素滴定を行った結果、複数の過酸化物や分解生成物を含有していることが考えられた。DMSOが過酸化物の発熱分解に与える影響を検討するため、THF試料にDMSOを混合し示差走査熱量測定(DSC)を用いて等温試験を行った結果、DMSO混合によりTHF過酸化物の発熱分解に要する時間が短縮した。反応機構が温度により変化しないと仮定し、活性化エネルギーを算出したところ、DMSO混合により活性化エネルギーが減少した。この結果は、過酸化物の発熱分解に要する時間がDMSOの存在下で短縮されることに矛盾しない。

\*横浜国立大学大学院環境情報学府

〒240-8501 神奈川県横浜市保土ヶ谷区常盤台79番7号

TEL: 045-339-3981 FAX: 045-339-4011

† Corresponding address: d10HF003@ynu.ac.jp