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HAZARD EVALUATION FOR OXIDATION OF CYCLIC ETHERS

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Ethers are widely used as a solvent for synthesis reactions, however, they are known as hazardous chemicals as they have low flash points and form peroxides under oxidative conditions. In this study, the oxidative reactivity of cyclic ethers was evaluated by thermal analysis. The accelerated test was performed in a pressure vessel under a high oxygen pressure (2 MPa), and DSC was used to detect the products of the reaction. Tetrahydrofuran (THF) and 1,3-dioxolane were used as a sample. The result of the DSC measurement of THF without any antioxidant showed that the DSC curve depended on the exposure time. It was found that this method can be used for the oxidation evaluation. The DSC measurement was also used for the detection of ether peroxides, and this method was faster and simpler than the potassium iodine titration.

Keywords: *1,3-dioxolane, oxidation, peroxide, tetrahydrofurane, thermal analysis*

Introduction

Ethers are widely used as a solvent for synthesis reactions, because of their high solvent power. In addition, most useful ethers have a low boiling point. However, they are known as hazardous chemicals in that they have low flash points and may form peroxides under oxidative conditions. For the hazard evaluation of oxidation, the oxidation induction time (OIT) is well-known. This method is used in the ASTM and other standards to determine the OIT of lubricating grease, plastics, etc., by a differential scanning calorimeter (DSC) [1, 2]. However, these methods can be used only for high boiling materials such as solids and pastes.

In this study, the oxidative reactivity of cyclic ethers was evaluated by thermal analysis. We carried out the measurement as an acceleration test using a high pressure vessel. This method kept a sample in a vessel under high oxygen pressure, and the oxidation was monitored by DSC. In order to quantitatively evaluate the auto-oxidation behavior, tetrahydrofuran (THF) and 1,3-dioxolane were thermally oxidized under a high oxygen pressure (2 MPa), and the thermal analysis was carried out to evaluate the effect of the antioxidants which prevented the oxidation. In addition, thermal and chemical analyses were performed to confirm the advantage of the thermal analysis. The hazard evaluation of oxidation by the DSC measurement was compared to the chemical analysis by potassium iodine (KI) titration.

Experimental

Materials

The materials used in this study were cyclic ethers. THF and 1,3-dioxolane are widely used as solvents for chemical reactions. Figure 1 shows their chemical structures. Generally, these materials contain an antioxidant to prevent oxidation. Both materials were used with and without the antioxidant. THF with an antioxidant contains 300 ppm di-*t*-butylhydroxytoluene (BHT). 1,3-dioxolane contains 75 ppm BHT, 100 ppm triethylamine or 100 ppm IRGANOX1010.

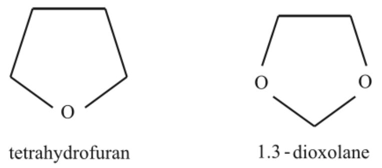

Fig. 1 The chemical formulas of cyclic ethers

Accelerated test

For oxidizing samples, we used the accelerated test with high pressure oxygen at isothermal condition. The accelerated test used a pressure resistant closed vessel. This spherical vessel was used as the sample vessel for the accelerated test which was made of stainless steel (SUS316). The inner volume was 10 mL. Approximately 2 mL of the sample was placed in the vessel with a 2 MPa oxygen atmosphere and then the vessel was placed in a drying oven. The

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drying oven was maintained at a predefined set temperature. The material was sampled at specific intervals and the thermal analysis was carried out.

In order to discuss the relationship between the results of the thermal analysis and the amount of oxygen adsorption, an accelerated test was carried out using a pressure resistant closed vessel with a pressure gauge. In addition, the effect of the sample vessel materials was investigated using three kinds of sample vessels i. e., SUS316, hastelloy c (HC) and titanium (Ti).

Potassium iodine titration

In order to determine the ether peroxide concentration, the KI titration was carried out. This method is used to quantify the concentration of hydroperoxide [3]. The sample was dissolved in an acetic acid and 2-propanol mixture and saturated KI was added. This mixture was heated and boiled for about 3 min. The liberated iodine was titrated with 0.1 N sodium thiosulfate solution.

Experimental apparatus

DSC

This study involved the thermal behavior of ether hydroperoxides using a DSC (TA Instruments DSC2920). In the experiment, nitrogen was used to purge in the DSC vessel. The high pressure sample cell, which was made of stainless steel (SUS303), was used. The sample mass was approximately 3 mg. The samples were heated from 30 to 300°C at the rate of 10 K min^{-1} and the onset temperature T_{DSC}/K and the heat of reaction Q_{DSC}/J g^{-1} were measured.

Results and discussion

Thermal behavior of THF

Figure 2 shows the DSC curve of THF which was sampled from the accelerated test in a 2 MPa oxygen atmosphere at 40°C. The exothermic reaction of THF without antioxidant was found to be at about 90°C and these T_{DSC} were 120 to 130°C. The Q_{DSC} increased with the increasing storage time. Figure 3 shows the heat of reaction of THF with and without antioxidant as a function of the storage time at 40°C. The maximum Q_{DSC} of THF was approximately 2000 J g^{-1} at 63 days. THF with antioxidant did not change the DSC profile. THF with antioxidant was stable for two months at 40°C.

Figure 4 shows the Q_{DSC} of THF with and without antioxidant as a function of the storage time at 60°C. The increase in the Q_{DSC} of THF without

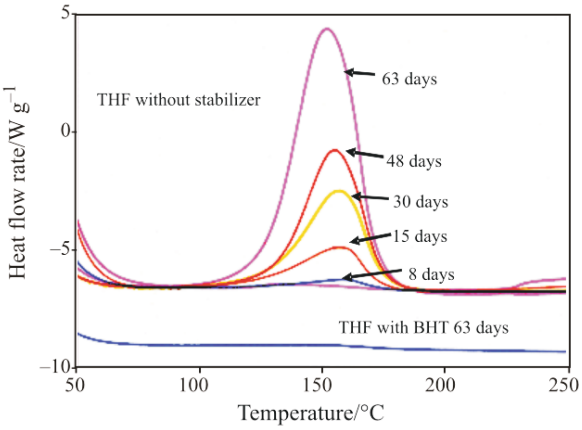

Fig. 2 The scanning DSC profile of THF which was sampled from the accelerated test at 40°C

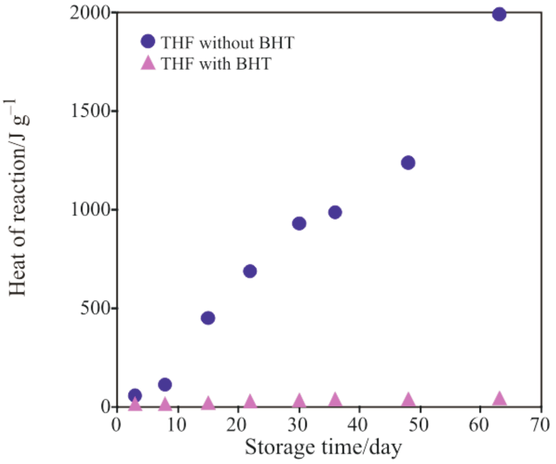

Fig. 3 The heat of reaction of THF as a function of storage time at 40°C

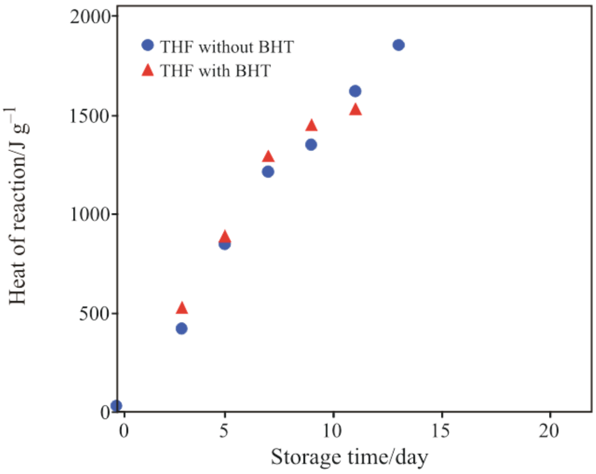

Fig. 4 The heat of reaction of THF as a function of storage time at 60°C

antioxidant at 60°C was 4 times faster than at 40°C. It showed the oxidation rate of THF was accelerated by the storage temperature. In addition, the Q_{DSC} of THF with antioxidant was increased at 60°C. The oxidation rate of THF with antioxidant was equal to that of THF without antioxidant. These results showed THF with antioxidant was unstable at high temperature.

Thermal behavior of 1,3-dioxolane

Figure 5 shows the DSC curves of the exothermic peak for 1,3-dioxolane with and without antioxidants. The exothermic reaction of 1,3-dioxolane was found to be at about 80°C and these T_{DSC} were 90 to 110°C. The Q_{DSC} increased with the increasing storage time. Figures 6 and 7 show the Q_{DSC} of 1,3-dioxolane with and without the antioxidant as a function of storage time at 30 and 40°C. The maximum Q_{DSC} of 1,3-dioxolane was approximately 1700 J g^{-1}. 1,3-dioxolane with the antioxidant was stable from a few days to one month. It was easy to be oxidized than THF. The antioxidant activity varied according to the antioxidants. IRGANOX showed a higher antioxidant activity than the others. Triethylamine had a significant effect on the storage temperature, and BHT had only a slight influence from 30 to 40°C.

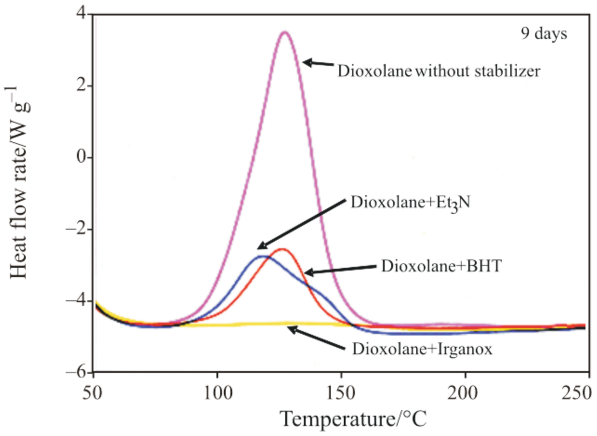

Fig. 5 The scanning DSC profile of 1,3-dioxolane which was stored at 30°C (9 days later)

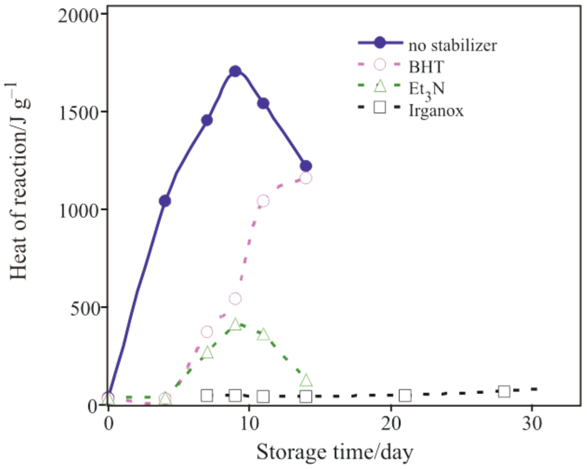

Fig. 6 The heat of reaction of 1,3-dioxolane as a function of storage time at 30°C

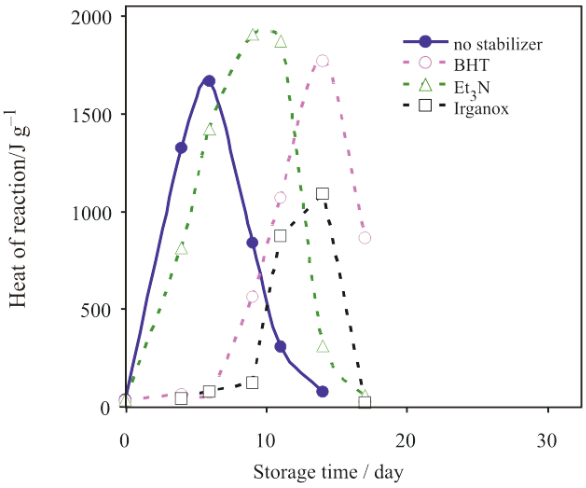

Fig. 7 The heat of reaction of 1,3-dioxolane as a function of storage time at 40°C

According to the results of the DSC measurement, the ether peroxide had a large heat of reaction and a low decomposition temperature, and the relationship of the rate of peroxide formation was different from the storage temperature and the antioxidants. Therefore, in order to evaluate the addition of the antioxidant to the ether, an accelerating test was used to measure at the operating temperature, because some antioxidants are sensitive to temperature like trimethylamine.

The above results indicate that to evaluate the oxidation behavior of cyclic ethers, one must evaluate to combine the thermal analysis and the accelerated test. This is useful for the evaluation of the stability of ethers and the performance assessment of an antioxidant for auto-oxidation.

Comparison of thermal and chemical analysis

In order to discuss the relationship between the thermal analysis and chemical analysis, the KI titration was performed. KI titration is known for the chemical quantitative analysis of hydroperoxide. This approach will allow us to discuss the advantage and limits of the DSC measurement. In addition, the relationship between the oxygen absorption during the accelerated test and the other analysis is discussed.

There were three kinds of sample vessels used for the accelerating test of THF. Figure 8 shows the heat of reaction of THF as a function of the storage time at 40°C. In the DSC measurement, THF per-

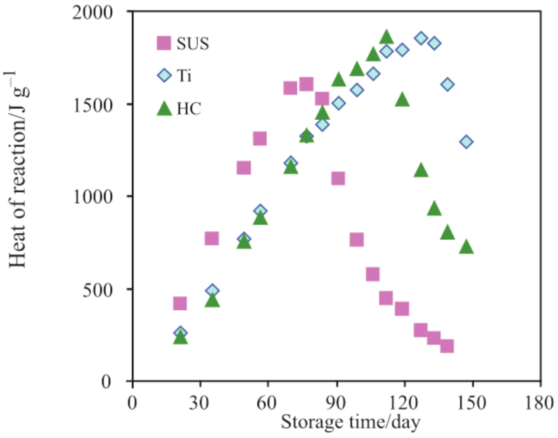

Fig. 8 The heat of reaction of THF as a function of storage time at 40°C

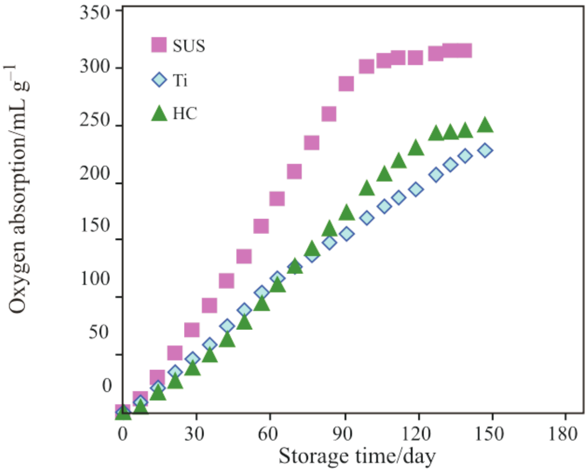

Fig. 9 The oxygen adsorption of THF as a function of storage time at 40°C

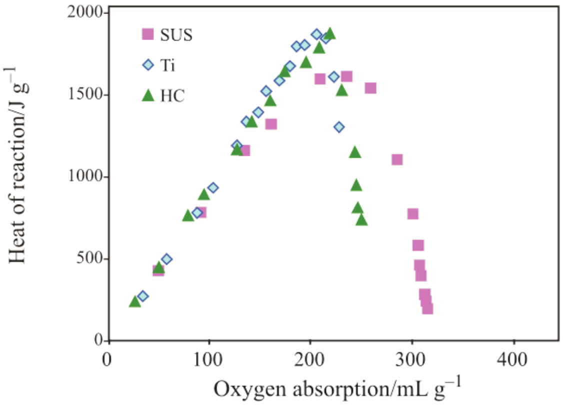

Fig. 10 The relationship between the oxygen adsorption and the heat of reaction of THF at 40°C

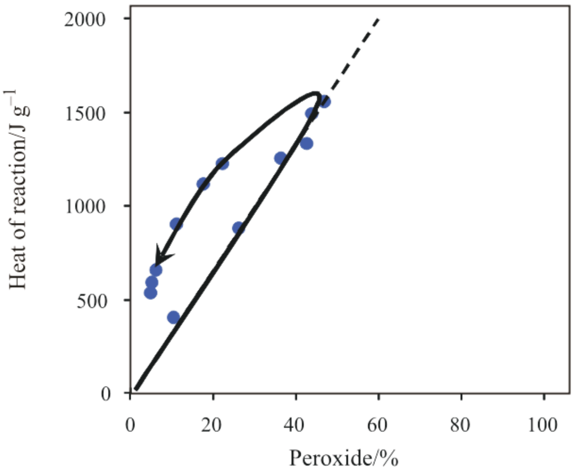

Fig. 11 The relationship between the concentration of peroxide determined by KI titration and the heat of reaction of THF at 60°C

oxides showed the effect by the sample vessel. The heat of reaction using the SUS vessel was faster than the Ti and HC vessels. The maximum Q_{DSC} of THF was found to be 1860 J g^{-1} at 112 days in the HC vessel from the beginning of the test, which then decreased. The Q_{DSC} of THF in the SUS vessel was lower and decreased faster than the others. SUS has a catalytic effect on the peroxide production and decomposition.

Figure 9 shows the oxygen absorption of THF as a function of the storage time. The oxygen absorption of THF increased with the increasing storage time. After the Q_{DSC} decreased, no increase in the oxygen absorption was observed. The relation between the oxygen absorption and the Q_{DSC} is shown in Fig. 10. This shows a good correlation with the oxygen absorption and the Q_{DSC} from the beginning of the test to the maximum Q_{DSC}. This result showed that the THF oxidation in the metal vessels was the same reaction, and only the rate of the reaction was catalyzed by the vessel material.

Figure 11 shows a comparison of peroxide concentration determined by the KI titration with the Q_{DSC} from the DSC measurement. This showed a good correlation with the peroxide concentration and the heat of reaction from the beginning of the test to the maximum Q_{DSC}. This result also showed that THF was converted to THF hydroperoxide by auto-oxidation, however, the behavior of the peroxide concentration was then different from that of the Q_{DSC}. The decrease in the peroxide concentration was faster than the Q_{DSC}. Therefore, the evaluation of the thermal hazard was lower by the KI titration at the high oxidation level. The product of the auto-oxidation reacted after a long time storage. THF hydroperoxide was changed to the other structure. Robertson reported the mechanism of the decomposition of THF hydroperoxide [4]. THF hydroperoxide was decomposed to γ-butyrolactone by thermal decomposition. Rein reported the reaction mechanism of the THF peroxide [5]. THF hydroperoxide formed alkylideneperoxide at a long storage time or under warm conditions. After the accelerated test, the samples of the liquid product were analyzed by gas chromatograph/mass spectrometry. The main product was γ-butyrolactone, and other carboxylic acids and alcohols were detected. These products were similar to the previous reports. KI titration cannot quantify other peroxides like the alkylideneperoxide, because this is the evaluation technique for hydroperoxides. Therefore, the evaluation of the titration was much lower than the thermal analysis after a long storage time.

Based on these above results, it is concluded that the accelerated test combined with the thermal analysis permits the quantitative evaluation of the autooxidation of cyclic ethers.

Conclusions

In order to evaluate the oxidation hazard of cyclic ethers, an accelerated test was performed, and the products were determined by thermal and chemical analyses. The results of the investigation are as follows:

- THF and 1,3-dioxolane easily produce peroxides in an oxidizing atmosphere. The stability of the ether was influenced by the antioxidants and storage temperature.
- There was a good relationship between the heat of reaction and the THF peroxide concentration with the increasing THF hydroperoxide concentration. After the THF hydroperoxide was converted to the other structure of the THF peroxide upon long time storage, the evaluation by the KI titration was lower than the thermal analysis.
- Accelerated oxidation test is a useful tool to evaluate the oxidation tendency of ethers. The DSC measurement is used for the determination of ether peroxides. It was faster and simpler than the KI titration.

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