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Thermal and oxidative stability of fluorinated alkyl aryl ethers

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Abstract

A series of compounds composed of hydrocarbon aryl components and fluorinated alkyl components joined by ether linkages were developed for evaluation as high performance lubricants. Thermal and oxidative stability of these compounds were evaluated. The basic molecular structure was shown to be highly durable against high temperature, even in air, which is an indispensable property if it is to be suitable as base stock for high performance lubricants. However, thermal and oxidative stability decreased when hydrogen atoms were present on carbons adjacent to benzene rings, especially in the case of the carbon at the center of the compound, which is adjacent to two benzene rings. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Thermal stability; Oxidative stability; Fluorinated alkyl aryl ethers; Synthetic lubricants

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1. Introduction

As performance and energy efficiency demands on mechanical apparatus are increasingly heightened, requirements for lubricant performance are becoming correspondingly demanding. Advanced aircraft and aerospace systems place extreme thermal and oxidative stress on lubricants, and maximum fluid temperatures in excess of 260°C (500°F) have been estimated for some future applications [1–2]. Improvements in the energy efficiency of automobile engines are also expected to require lubricants which are highly durable at high temperature [3–4]. Air conditioner and refrigeration systems also require oil with exceptional thermal stability [5] in addition to solubility with refrigerants.

Although some conventional lubricants and recently developed candidate fluids have excellent thermal stability, each of them have certain drawbacks which inhibit their widespread adoption. Fluorinated polyethers have excellent thermal and oxidative stability up to 370°C as well as good lubricating properties [6–9], but high production costs limit their use. Polyphenylether have excellent thermal and oxidative stability also [10], but they exhibit poor lubricating properties [3,11] and poor wetting characteristics [12]. Esters and silicones are not oxidatively stable at 260°C [13]. Silahydrocarbons are reported to have superior thermal stability and good viscosity properties [1], but their relatively high production costs limit their use [14,15].

Fluorinated alkyl aryl ethers are considered to be suitable for base stock of high performance lubricants because they are expected to have (a) high stability, (b) good lubricity, and (c) good miscibility with conventional additives for hydrocarbon base stock (Fig. 1). In this study, the thermal and oxidative stability of a series of novel fluorinated alkyl aryl ethers developed as candidates for base stock of high performance lubricants were investigated.

2. Experimental

2.1. Synthesis of fluorinated alkyl aryl ethers

The fluorinated alkyl aryl ethers investigated in this study were synthesized as follows.

2.1.1. Synthesis of 2,2-bis[4-(1,1,2,2-tetrafluoroethoxy)-phenyl]propane (hereinafter reffered to as "BisA-TFE")

A solution consisting of 68.7 g of 2,2-bis(4-hydroxyphenyl)propane (hereinafter reffered to as "bisphenol A") and 6.2 g of potassium hydroxide dissolved in 120 ml of dimethyl sulfoxide was charged into a 500 ml microcylinder. The cylinder was degassed, charged with N_2 gas to restore atmospheric pressure, and then heated to 60°C by means of an oil bath. Tetrafluoroethylene was then introduced to initiate a reaction. The reaction was carried out for about

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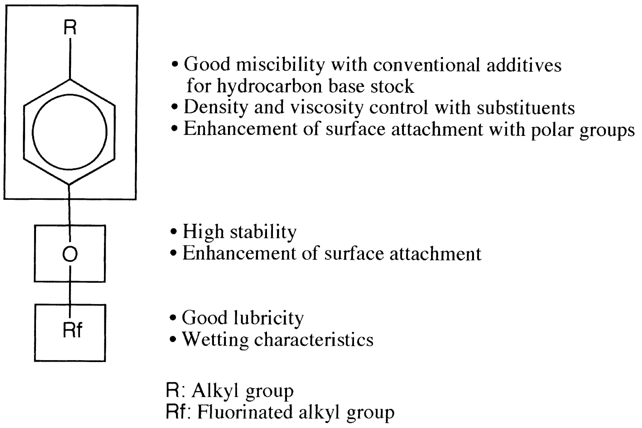


Fig. 1. Rationale for selection of fluorinated alkyl aryl ether as candidates for base stock of high performance lubricants (R: alkyl group; Rf: fluorinated alkyl group).

5 h with tetrafluoroethylene fed in to maintain reactor pressure between 3 and 4 kg/cm^2.

After completion of the reaction, reaction product was obtained by distilling off dimethyl sulfoxide at 80°C under about 5 mm Hg, and 500 ml of 1,1,2-trichloro-1,2,2-trifluoroethane (hereinafter reffered to as "CFC-113") was added to the reaction product obtained. This CFC-113 phase was washed three times with 500 ml of distilled water, and CFC-113 was removed off under reduced pressure. Thus, 130 g of colorless, transparent oil was obtained. The main fraction (118 g) was isolated by simple distillation, at a boiling point of about 150°C under about 0.1–0.3 mm Hg, indicating that the yield was 92%.

The isolated fraction was analyzed by infrared absorption spectrometry and mass spectrometry [*m*/*e* 428 (M^+), 413 ($M^+{-}CH_3$)] to confirm that the fraction was BisA-TFE, having the structural formula shown in Fig. 2.

2.1.2. Synthesis of 1,1,3,3-tetramethyl-4-(1,1,2,2-tetrafluoroethoxy)phenylbutane (hereinafter reffered to as "PTOP-TFE")

PTOP-TFE was prepared in substantially the same manner as BisA-TFE except that *p-tert*-octylphenol (obtained from Tokyo Kasei Kogyo) was used in place of bisphenol A. The yield was 94%. Infrared absorption spectrometry and mass spectrometry [*m*/*e* 306 (M^+)] confirmed that the obtained product was PTOP-TFE, having the structural formula shown in Fig. 2.

2.1.3. Synthesis of 2,2-bis[4-(1,1,2,2-tetrafluoroethoxy)-phenyl]-4-methylpentane (hereinafter reffered to as "MIBK-Bis-TFE")

MIBK-Bis-TFE was prepared in substantially the same manner as BisA-TFE except that 2,2-bis(4-hydroxyphenyl)-4-methylpentane (obtained from Honshu Chemical) was used in place of bisphenol A. The yield was 95%. Infrared absorption spectrometry and mass spectrometry [*m*/*e* 470

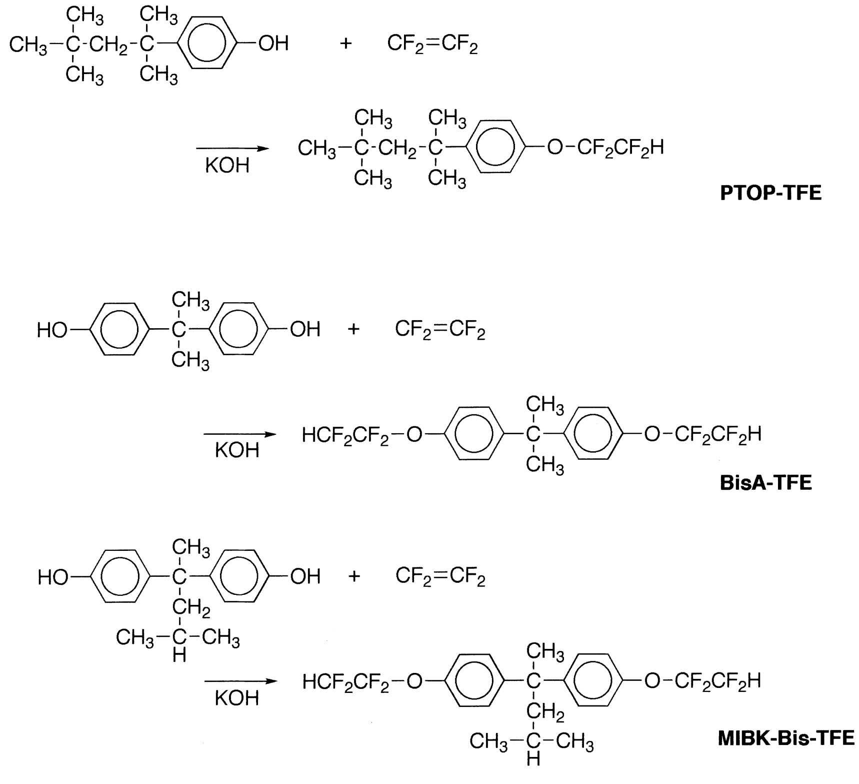


Fig. 2. Structure and synthesis of fluorinated alkyl aryl ethers.

(M^+)] confirmed that the obtained product was MIBK-Bis-TFE, having the structural formula shown in Fig. 2.

2.1.4. Synthesis of BisP-OT-TFE, BisOTBP-A-TFE, BisOSBP-A-TFE, BisTOP-F-TFE, BisP-IOTD-TFE and TMBisA-TFE

These compounds were prepared in substantially the same manner as BisA-TFE, except that 2,2-bis(4-hydroxyphenyl)-octane, 2,2-bis(3-*tert*-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-*sec*-butyl-4-hydroxyphenyl)propane, bis(*tert*-octylhydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)-2-ethylhexane, and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane were used in place of bisphenol A. Each of these materials were obtained from Honshu Chemical, except bis(*tert*-octylhydroxyphenyl)methane, which was obtained from Asahi Organic Chemicals. Yields were 90%, 91%, 94%, 95%, 88%, and 46%, respectively. Infrared absorption spectrometry and mass spectrometry confirmed that the products were compounds having the structural formulas shown in Table 2.

2.2. Evaluation of thermal and oxidative stability

Thermal and oxidative stability of the fluorinated alkyl aryl ethers were measured, and their results were compared with those obtained for commercially available lubricants.

2.2.1. Commercially available lubricants

Three types of perfluoropolyether oils, as below, were studied.

Fluid K: $C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5.$
Fluid F: $CF_3O[CF(CF_3)CF_2O]_m(CF_2O)_nCF_3.$
Fluid D: $C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5.$

Fluid K was obtained from DuPont (Krytox 143AB), Fluid F was obtained from Montefluos (Fomblin Y25A) and Fluid D was obtained from Daikin Industries (Demnun S-65).

Two typical polyphenylethers were obtained from Matsumura Oil Research: *m*-bis(*m*-phenoxyphenoxy)benzene (S-3105), and monoalkyl-*m*-phenoxy-*o*-biphenyl (S-3101). Dimethylsilicone (KF96-100cSt), phenylmethylsilicone (KF-54) and fluorinated silicone (X-22-822) were obtained from Shin-Etsu Chemical. Branched alkylbenzene (Aromix 20T) was obtained from Nippon Petroleum Detergent.

2.2.2. Measurement of decomposition temperature

Decomposition temperatures were investigated using a high-pressure differential scanning calorimeter manufactured by Rigaku. Sample temperatures were raised in the order of 5°C/min up to 400°C. Decomposition temperatures were determined by observing the predominant slope of the first peak to appear, and extending a line from this slope back to the baseline, as shown in Fig. 3.

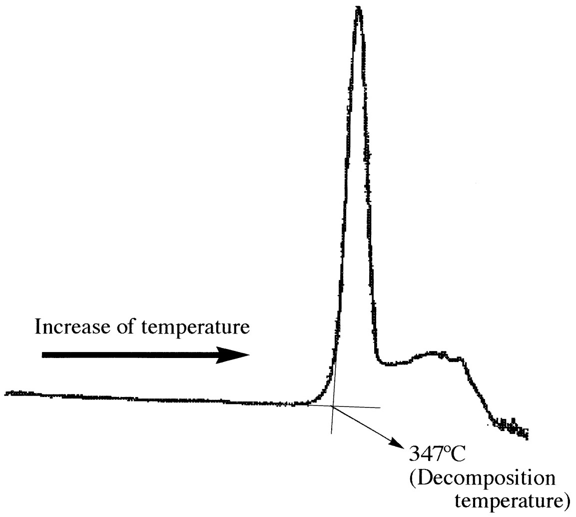


Fig. 3. High-pressure DSC chart of BisA-TFE.

2.2.3. Measurement of total acid number (TAN) and degree of decomposition

Specimens were heated to 175°C for 19 h in an atmosphere of N_2 with 1 wt% O_2, standard conditions for a preliminary test of stability for refrigeration system lubricants. TAN was then measured in substantially the same manner as ISO 6618, except that 0.01 mol/l solution of potassium hydroxide was used in place of 0.1 mol/l solution. Degree of decomposition was determined through gas chromatography, expressed by area of peaks of thermal decomposition products as percentage of total gas chromatograph area.

3. Results and discussion

3.1. Thermal and oxidative stability of the basic molecular structure

Fig. 4 shows the basic molecular structure of the fluorinated alkyl aryl ethers studied. It consists of a hydrocarbon aryl moiety, a fluorinated alkyl moiety and an ether linkage group. In order to evaluate thermal and oxidative stability of this basic molecular structure, BisA-TFE, PTOP-TFE, and MIBK-Bis-TFE (shown in Fig. 2) were prepared by nucleophilic additions of tetrafluoroethylene (TFE) to alkylphenol or bisphenols.

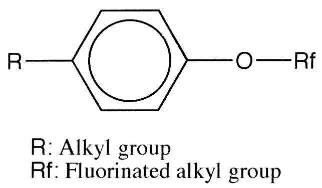


Fig. 4. Basic molecular structure of fluorinated alkyl aryl ether (R: alkyl group; Rf: fluorinated alkyl group).

Table 1
Decomposition temperature of fluorinated alkyl aryl ethers and conventional high performance lubricants

Sample	Viscosity[a] (cSt at 40°C)	Decomposition temperature (°C)[b]	
		In air	In N_2
Fluorinated alkyl aryl ether			
BisA-TFE	26	347	>400
PTOP-TFE	6	300	>400
MIBK-Bis-TFE	109	290	>400
Perfluoropolyether			
Fluid D[c]	65	388	>400
Fluid K[d]	86	384	367
Fluid F[e]	94	375	>400
Polyphenylether			
m-bis(*m*-phenoxyphenoxy)benzene (S-3105)	266	352	>400
Monoalkyl-*m*-phenoxyphenoxy-*o*-biphenyl (S-3101)	243	210	>400
Silicone oil			
Dimethylsilicone (KF96-100cSt)	100	252	>400
Phenylmethylsilicone (KF-54)	400	345	>400
Fluorinated silicone (X-22-822)	100	235	247

[a] Measured with E-type rotational viscometer (Tokyo Keiki).

[b] Measured with high-pressure DSC (Rigaku).

[c] Demnum S-65, manufactured by Daikin.

[d] Krytox 143AB, manufactured by E.I. DuPont De Nemours.

[e] Fomblin Y25A, manufactured by Nippon Montedison K.K.

Table 1 shows decomposition temperatures that resulted from high-pressure DSC analysis. In addition to these three fluorinated alkyl aryl ethers, a representative range of perfluoropolyethers, polyphenylethers, and silicone oils, which are conventionally used as lubricants in extreme heat conditions, were also evaluated.

In nitrogen, fluorinated silicone was the only sample which showed an exothermic peak below 400°C. In contrast, all samples showed exothermic peaks under 400°C in air, indicating oxidative decomposition. Monoalkyl-*m*-phenoxyphenoxy-*o*-biphenyl, fluorinated silicone, and dimethyl silicone were shown to be the least resistant to oxidative decomposition, with decomposition temperatures of 210°C, 235°C, and 252°C, respectively.

The fluorinated alkyl aryl ethers proved to be quite stable against high temperatures, with none of the samples showing endothermic or exothermic peaks below 400°C in nitrogen, while exothermic peaks in air were observed at 300°C, 347°C, and 290°C for PTOP-TFE, BisA-TFE, and MIBK-Bis-TFE, respectively, all higher oxidative decomposition temperatures than observed with monoalkyl-*m*-phenoxyphenoxy-*o*-biphenyl, fluorinated silicone and dimethyl silicone. These results indicated that the basic fluorinated alkyl aryl ether molecular structure studied was highly durable against high temperature, even in air.

3.2. Effect of substituents on thermal and oxidative stability

In order to evaluate the effect of alkyl-group substituents on the thermal and oxidative stability of BisA-TFE, a series of compounds were prepared, and tested at 175°C for 19 h in N_2 containing 1 wt% O_2. Table 2 shows changes in TAN and degree of decomposition.

Both change in TAN and degree of decomposition for BisA-TFE and MIBK-Bis-TFE were very slight, indicating good stability under these test conditions. BisOTBP-A-TFE, BisOSBP-A-TFE and TMBisA-TFE are compounds with *tert*-butyl groups, *sec*-butyl groups and methyl groups, respectively, substituted on the benzene rings of BisA-TFE. BisOTBP-A-TFE, with *tert*-butyl group substitutions, displayed TAN and decomposition results similar to BisA-TFE. BisOSBP-A-TFE, with *sec*-butyl group substitutions, showed slightly more decomposition, but similar TAN results. In contrast, TMBisA-TFE, with methyl group substitutions, showed a TAN increase to 1.26 mg KOH/g and 3.62% decomposition.

These results suggest that thermal and oxidative stability is related to the presence of hydrogen atoms on carbon atoms adjacent to the benzene rings. Such carbons appear to be susceptible to oxidation under high temperature. Gas chromatography–mass spectroscopy analysis of post-test sample from BisOSBP-A-TFE revealed a peak at 526 *m*/*e*. It is believed that this peak corresponds to an oxidation product with the structure shown in Fig. 5, with the oxidation occurring at one of the carbons adjacent to a benzene ring.

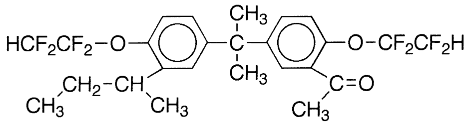


Fig. 5. Proposed structure for decomposition product of BisOSBP-A-TFE.

Table 2
Stability of substituted fluorinated alkyl aryl ether at test condition: 175°C, 19 h in N_2 containing 1 wt% O_2

Compounds	Viscosity[b] (cSt at 40°C)	TAN(mg KOH/g)		Degree of decomposition[a] (% GC area)
		Before test	After test	
BisA-TFE	26	<0.01	0.01	<0.01
MIBK-Bis-TFE	109	<0.01	<0.01	<0.01
BisP-OT-TFE	112	<0.01	0.02	0.04
BisOTBP-A-TFE	(Solid)	<0.01	<0.01	<0.01
BisOSBP-A-TFE	91	<0.01	0.01	0.03
BisTOP-F-TFE	1789	<0.01	0.25	2.06
BisP-IOTD-TFE	250	<0.01	0.35	2.14
TMBisA-TFE	(Solid)	<0.01	1.26	3.62
Branched alkyl benzene [c]	14	<0.01	1.55	–

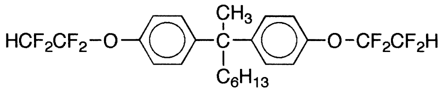
[a] Gas chromatography (area % of peaks for thermal decomposition products, based on the total area of chromatogram).

[b] Measured with E-type rotational viscometer (Tokyo Seiki).

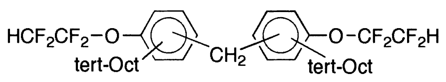
[c] Aromix 20T (Nippon Petroleum Detergent)

Test Condition: 175°C 19 hrs in N2 containing 1 wt.% O2
*1: gas choromatography (area % of peaks for thermal decomposition products, based on the total area of chromatogram)
*2: measured with E-type rotational viscometer (Tokyo Seiki)
*3: Aromix 20T (Nippon Petroleum Detergent)

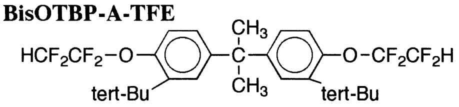
BisP-OT-TFE



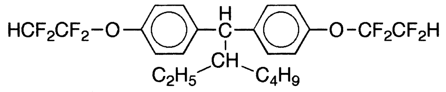
BisTOP-F-TFE



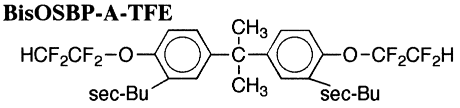
BisOTBP-A-TFE



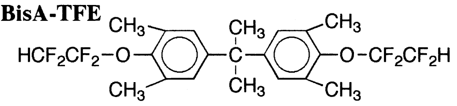
BisP-IOTD-TFE



BisOSBP-A-TFE



TMBisA-TFE



BisP-OT-TFE, a compound with an *n*-hexyl group substituted on the central carbon of BisA-TFE, turned out to be highly stable under the test conditions. Both BisTOP-F-TFE, with two hydrogen atoms on the central carbon and *tert*-octyl groups substituted on the benzene rings, and BisP-IOTD-TFE, with one hydrogen atom and one 1-ethyl pentyl group on the central carbon, displayed TAN and decomposition results which indicate susceptibility to oxidative decomposition. It is believed that BisTOP-F-TFE and BisP-IOTD-TFE were highly susceptible to oxidation due to the presence of hydrogen atoms on the central carbon, which is adjacent to benzene rings on two sides.

4. Conclusions

These results suggest the following conclusions: (1) the basic molecular structure of fluorinated alkyl aryl ethers has excellent oxidative and thermal stability, but (2) thermal and oxidative stability decreases when hydrogen atoms are present on carbon atoms adjacent to benzene rings.

These conclusions will serve as a useful guide to maintain stability while introducing various substituent groups to fluorinated alkyl aryl ethers in order to improve other properties. In subsequent studies, the authors will evaluate lubricity and other properties of fluorinated alkyl aryl ethers for use as lubricants.

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