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The Preparation of New Perfluoroether Fluids Exhibiting Excellent Thermal-Oxidative Stabilities

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THERMAL-OXIDATIVE STABILITIES

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SUMMARY

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A series of low molecular weight perfluoroalkylethers (PFAE) were synthesized by direct fluorination. Viscosity-temperature properties and oxidation stabilities were determined. Viscosity-temperature correlations indicated that increases in branching and increases in the size of the branching substituent caused a deterioration in viscometric properties (i.e., an increase in ASTM slope). In addition, increasing the ratio of carbon to oxygen in these compounds also increased the ASTM slope. Preliminary oxidation stability measurements indicated that highly branched PFAE fluids (i.e., those containing quaternary carbons) may be less stable than either those containing a single trifluoromethyl pendant group or those containing no branching at all.

INTRODUCTION

Perfluoroalkylethers are a class of fluids which exhibits excellent thermal and oxidative stability (refs. 1 to 3) and when combined with good viscosity-temperature characteristics (ref. 3), good elastohydrodynamic film forming capabilities (ref. 5), good boundary lubricating ability (refs. 3 to 6), and nonflammability properties (ref. 7) make these fluids promising candidates for high temperature lubricant and hydraulic fluid applications.

The performance of perfluoropolyethers depend heavily on the molecular architecture of the compound. Only several molecular structures are presently available using existing technology. Du Pont produces telomers and polymers of hexafluoropropylene oxide (Krytox) by the anionic polymerization of hexafluoropropylene oxide monomer (ref. 8). An Italian company, Montecatini Edison, manufactures a series of polymers known as Fomblins which contain varying amounts of difluoromethylene oxide in the polymer chain. Fomblin Z is prepared using an ultraviolet light activated polymerization of tetrafluoroethylene in the presence of oxygen (ref. 9). This polymer is primarily a random copolymer of difluoromethylene oxide and tetrafluoroethylene oxide.

However, both of these commercial fluids have deficiencies. The Krytox fluids have superior oxidation stability but very poor viscosity temperature properties (refs. 4 and 10). On the other hand, the Fomblin Z fluids exhibit

excellent viscosity properties but poorer high temperature stability (refs. 4 and 11). Both fluids are catalytically degraded in the presence of certain metal alloys (refs. 10 to 12). However, oxidation inhibitors can result in substantial improvements (refs. 12 and 13).

A recent entry into the unbranched PFAE arena is a series of fluids (Demnum) manufactured by Daikin Industries, LTD in Japan. These fluids, which are apparently made via a polymerization process, are based on a propane repeating unit. Little is known about their high temperature properties but their viscosity-temperature behavior lies between that of Krytox and Fomblin Z.

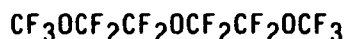
Recently, the use of direct fluorination has been very successful in producing perfluoropolyethers as well as a variety of other fluorinated compounds (ref. 14). Not only can perfluoropolyethers often be made in a single-step reaction with much cheaper starting materials, but the process is extremely versatile with the availability of the hydrocarbon precursor being the primary limiting factor. For example, highly branched ethers can be made using direct fluorination, as well as novel polyethers containing more than two sequential carbon atoms in the polymer chain-structures which cannot be made using conventional techniques.

Therefore, the objective of this work was to synthesize several novel perfluoropolyether model compounds via direct fluorination and then to correlate their viscosity and oxidation characteristics with their respective structures.

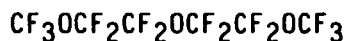
EXPERIMENTAL SECTION

Six model perfluoropolyether compounds were selected for synthesis. Their names and structures, as well as the polymers they model, appear in Table I. A seventh compound (hexafluoropropylene oxide hexamer) was included in this study for comparison and was kindly supplied by the Du Pont Co. The synthetic procedures used to synthesize the model compounds are as follows:

1. Perfluorodiglyme

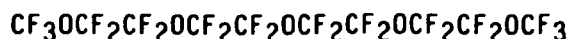


10 g diglyme (b.p. 162 °C) was placed in a nickel boat. The boat was placed in a 5.1 cm (2 in.) i.d. by 30.5 cm (12 in.) long reactor which was purged with 200 cc/min nitrogen for several hours prior to beginning the reaction. The fluorine flow was set at 10 cc/min and was held at that level until the reaction was complete as indicated by a drop in reactor temperature. The product was collected in a trap downstream from the reactor which was held at -50 °C. The product, perfluorodiglyme (10.4 g), was obtained in greater than 99 percent purity by an atmospheric distillation of the products in the trap. b.p. 65 to 66 °C, m.w. 386, yield 36 percent, ^{19}F nmr (84.87 MHz, neat) δ 58.7 (t,a), 93.7 (q,b), 91.7 ppm (s,c).



a b c

2. Perfluorotetraglyme

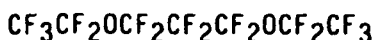


Perfluorotetraglyme can be prepared in 45 percent yield by fluorinating 10 g of tetraglyme (b.p. 275 °C) using the procedures described for the fluorination of diglyme, 12.5 g of perfluorotetraglyme (b.p. 138 °C) was obtained in greater than 99 percent purity following an atmospheric distillation of the products collected in the trap. m.p. -70 °C, m.w. 618, ¹⁹F nmr (84.87 MHz, neat) δ 58.7 (t,a), 93.3 (q,b), 91.2 ppm (s,c).



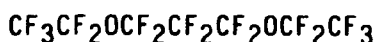
a b c

3. Perfluoro(1,3-diethoxypropane)



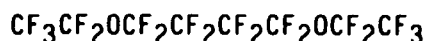
30.4 g of 1,3-propanediol (0.4 mol) was added dropwise at room temperature to a vigorously stirred suspension of sodium hydride 20.4 g (0.85 mol) in 1000 ml tetrahydrofuran (dried over calcium hydride). The mixture was refluxed for 30 min. Diethylsulfate 111 ml (0.85 mol) was added slowly to the refluxing mixture over a 2 hr period. The mixture was refluxed an additional 2 hr then cooled to room temperature. Water (500 ml) was added to the product mixture and the aqueous and organic layers were separated. The aqueous layer was extracted twice with methylene chloride and the combined extracts were dried over sodium sulfate. The solvents were removed by distillation and the resulting oil was vacuum-distilled to give 1,3-propanediol-diethylether 39.6 g (60 percent yield).

10 g 1,3-propanediol-diethylether (b.p. 40 °C/12 mm) was fluorinated with 10 cc/min F₂ in a two day fluorination reaction. The resulting product, perfluoro(1,3-diethoxypropane) 11.5 g was obtained in 36 percent yield. Distillation of the product mixture resulted in a product with 99 percent purity. b.p. 75 to 76 °C, m.w. 420, ¹⁹F nmr (84.87 MHz, neat) δ 90.4 (s,a), 91.3 (m,b), 86.1 (m,c), 132 (s,d).



a b c d

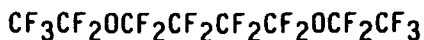
4. Perfluoro(1,4-diethoxybutane)



Sodium hydride powder 20.4 g (0.85 mol) was suspended in 1000 ml tetrahydrofuran in a 2 liter flask. To this mixture 1,3-butanediol 36.0 g (0.4 mol) was added slowly at room temperature with vigorous stirring. The mixture was allowed to reflux for 30 min at which time diethylsulfate 111 ml (0.85 mol) was added slowly over a 2 hr period. The mixture was refluxed for an additional 2 hr, water 500 ml was added, and the aqueous phase was separated from the organic layer in a separatory funnel. The aqueous layer was extracted twice with methylene chloride and the combined extracts were dried over sodium

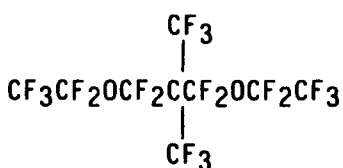
sulfate. The crude product was vacuum-distilled following removal of the solvent via an atmospheric distillation to give 1,4-butanediol-diethylether 41 g (71 percent yield).

10 g 1,4-butanediol-diethylether (b.p. 58 °C/12 mm) was fluorinated with 10 cc/min fluorine in a typical two day reaction. The volatile product, perfluoro(1,4-diethoxybutane) 11.9 g was obtained in 37 percent yield. b.p. 96 °C, m.w. 470, ¹⁹F nmr (84.87 MHz, neat), δ 90.3 (s,a), 91.3 (q,b), 86.0 (m,c), 128.7 ppm (t,d).



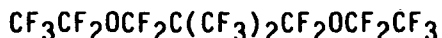
a b c d

5. Perfluoro(1,3-diethoxy-2,2-dimethylpropane)



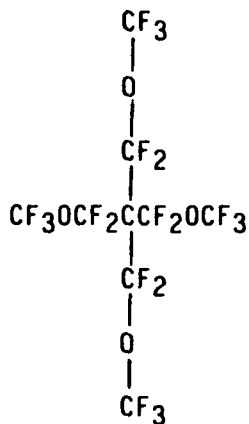
The fluorination of 1,3-diethoxy-2,2-dimethylpropane gives the above perfluoro compound in moderate yield. The hydrocarbon starting material can be made in 70 percent yield using the procedure described for the preparation of perfluoro(1,4-diethoxybutane). 2,2-dimethyl-1,3-propanediol 42 g (0.4 mol) is reacted with 20.4 g sodium hydride (0.85 mol) and 111 ml diethylsulfate (0.85 mol). Extraction of the aqueous layer with methylene chloride gave 45 g 1,3-diethoxy-2,2-dimethylpropane (b.p. 67 °C/40 mm).

Fluorination of the compound (10 g) using the procedures described for the fluorination of diglyme gave 12.4 g perfluoro(1,3-diethoxy-2,2-dimethylpropane) (38 percent yield). b.p. 85 °C, m.w. 520, ¹⁹F nmr (84.87 MHz, neat) δ 90.3 (s,a), 91.7 (m,b), 69.7 (m,c), 66.3 ppm (p,d).



a b c d

6. Perfluoro(pentaerythrityl)tetramethyl ether



Pentaerythrityltetramethyl ether can be prepared using the reaction described for the ethyl-capped ethers with one exception - dimethylsulfate is used as the alkylating agent in place of diethylsulfate (34.6 g, 45 percent yield, b.p. 80 °C/7 mm). Fluorination of the material (10 g) gave 9.5 g perfluoro-(pentaerythrityltetramethyl ether). Yield 33 percent, b.p. 95 °C, m.w. 552, ¹⁹F nmr (84.87 MHz, neat) δ 58.5 (s,a), 70.8 ppm (s,b).



a b

Viscosity-Temperature Measurements

Standard cannon-manning semi-micro capillary viscometers were used for all kinematic viscosity measurements. Measurements were made in a constant temperature bath at temperatures of 38 °C (100 °F) and 54 °C (130 °F). All data were plotted on standard ASTM rectifying charts and the viscosity-temperature slope (ASTM slope) determined from the resulting straight lines. These data appear in figure 1 and are tabulated in table II.

Thermal-Oxidative Degradation Measurements

Degradation measurements were made on each fluid (except perfluorodiglyme) at 360 °C in oxygen for 48 hr. The degradation apparatus is shown schematically in figure 2. It consists of a pyrex glass ampule into which a pre-weighed amount of each compound was condensed. With liquid nitrogen touching only the bottom of the ampule, 100 mm of oxygen was introduced into the tube. The ampule was then sealed using a propane torch and placed in a box furnace for 48 hr. Temperature was maintained at 360 °C ± 1° for the duration of the experiment.

After removal from the furnace, the tube was allowed to cool to room temperature and was attached to a flexible vinyl tube using a 1.27 cm (0.5 in.) Ultratorr union. The other end of the vinyl tube was affixed to a vacuum line using a second union. Following evacuation of the vinyl tube, the ampule was opened by bending the vinyl tube until the tube of the ampule broke. The contents of the ampule were condensed into a liquid nitrogen-cooled trap. The contents of the trap were slowly passed through a -95 °C trap (toluene slush) and the portion passing the -95 °C trap was collected and weighed. A percent decomposition was calculated based on the amount of volatiles formed. Tests were repeated at least three times and an average decomposition rate calculated. These data appear in figure 3 and are tabulated in table III.

RESULTS AND DISCUSSION

A comprehensive structure-property study for the development of a high temperature liquid lubricant should include the following correlations: (1) viscosity-temperature, (2) thermal-oxidative stability, (3) friction and wear, (4) metal-elastomer compatibility, (5) compressibility, and (6) toxicity. Since this was a preliminary study, only the first two correlations will be addressed.

Viscosity-Temperature

In order to function as a high temperature lubricant, a fluid must have a wide liquid range. That is, it must possess good low temperature fluidity while retaining low volatility at high temperatures. Snyder et al. (ref. 4) have shown that the commercial hexafluoropropylene oxide fluids (HFPO) do not possess a wide liquid range due to their steep viscosity-temperature slope. They also showed that the linear perfluoroalkylethers (PFAE) do possess a wide liquid range but at a sacrifice in high temperature oxidation stability. Therefore, the overall goal of this work is to produce a material with viscosity properties equivalent to the linear PFAE fluids but with oxidation stability equal to or surpassing that of the HFPO fluids.

Viscosity-temperature correlations are usually made by use of rectifying charts produced by the American Society for Testing and Materials (ASTM). When kinematic viscosities are plotted on these charts as a function of temperature, straight lines are normally produced. The charts are based on the empirical MacCoull-Walther equation (ref. 15). It relates the kinematic viscosity (ν) in centistokes (cS) to the absolute temperature (T) as follows:

$$\log \log Z = A - B \log T \quad (1)$$

where:

$$Z = \nu + 0.7 + C$$

A and B = constants

A and B are two parameters which characterize the viscosity-temperature behavior. The constant C is adjusted based on viscosity level. The use of these charts appears in ASTM test method D-341-77 (ref. 16).

The charts were designed to be used with hydrocarbons and petroleum fluids. Sometimes synthetic fluids do not produce straight lines on these charts. However, over the temperature range of this study, this is not a problem.

Viscosity information generated in the past on commercial perfluorinated fluids utilized charts from a previous ASTM to standard (D-341-43). With these charts, viscosity temperature behavior was correlated using a parameter called the ASTM slope. This parameter was obtained by physically measuring the slope on the charts. It should be pointed out that this slope is not numerically equivalent to the slope B in equation (1). Therefore, all of the correlations in this paper use the ASTM slope.

Viscosity temperature behavior for the model compounds appears in figure 1. Measurements were made at 38 °C (100 °F) and 54 °C (130 °F). These data and the ASTM slopes are tabulated in table II.

One problem should be pointed out in comparing the ASTM slopes. The viscosity level (or molecular weight) affects the slope as well as differences in chemical structure. This is clearly illustrated in figure 4 where the ASTM slope is plotted as a function of molecular weight for a series of branched perfluoroalkylethers (Krytox and Fomblin Y fluids). As can be seen, the effect

is greater at low molecular weights than at higher values. Since all of the model compounds had molecular weights less than a 1000 and each was different, it makes comparisons somewhat difficult. Figure 5 is a similar plot of slope as a function of molecular weight for some unbranched fluids (Fomblin Z and Demnum fluids).

Effect of Branching

As mentioned earlier, it is well known that the branched Krytox fluids, which have pendant trifluoromethyl groups, have much poorer viscosity-temperature behavior than the unbranched Fomblin Z fluids. For example, the Krytox AX fluid has a MW of 4800 and a slope of 0.63. A fluid of comparable viscosity at 38 °C, Fomblin Z15, has a MW of 9500 and a slope of only 0.30. A comparison of the two series appears in Fig. 5.

The HFPO hexamer, which is essentially a lower MW homolog of the Krytox series is included in figure 4. Not surprisingly, it falls on the same curve. The two highly branched model compounds are also plotted in this figure. If one draws a tangent to the curve and extrapolates to zero MW, the diethoxy dimethylpropane compound falls above the line. This fluid is more highly branched since it has two pendant trifluoromethyl groups compared to one for the HFPO series of fluids. The pentaerythritol ether shows much worse viscosity-temperature properties as it lies well above the extrapolated line. This fluid contains the more bulky perfluoro-(methoxymethylene) groups. Therefore, one may conclude that as the amount of branching and the size of the substituent increases, the viscosity-temperature behavior will be adversely affected.

Effect of Carbon to Oxygen Ratio

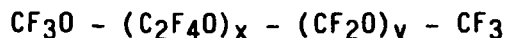
Another factor which will affect viscosity-temperature properties is the ratio of carbon to oxygen in the polymer backbone. Figure 6 contains viscosity-temperature slope as a function of carbon to oxygen ratio in a series of unbranched PFAE. These compounds are relatively low MW and some are end capped with $-CF_3$ while others with $-C_2F_5$. Therefore, the C/O ratio used in this correlation is calculated for the entire compound rather than just in the polymer repeating unit. Two of the compounds (E and F) are from reference 17, while the remaining four are model compounds synthesized in this program.

As can be clearly seen in figure 6, increasing the C/O ratio adversely affects viscosity-temperature slope. For example, we can compare two compounds of essentially the same MW (compounds D and F). These compounds have similar structure, except F has an extra ether linkage. D has a C/O ratio of 4 while F has a ratio of 2.7. Their respective slopes are 1.61 and 1.05. In addition, the extra ether linkage causes a decrease in viscosity. At 38 °C, D has a viscosity of 0.61 cS while F has a value of 0.53 cS.

Presumably, the decrease in viscosity and viscosity-temperature slope with decreasing C/O ratio is due to freer internal rotation about the carbon-oxygen bond compared to that of a carbon-carbon bond. However, this can not be the sole reason since it has been reported (ref. 17) that ether linkages also reduce viscosities and slopes for perfluoro cyclic ethers as well as in

perfluoro straight chain monoethers. Since free rotation is not possible in the cyclic compounds, another factor must be responsible for this effect.

At any rate, this correlation indicates that a fluid having the lowest C/O ratio would have the best viscometric properties. The fluid containing the lowest C/O ratio of 1 would be a perfluorinated polymethylene oxide. Commercial fluids coming closest to this structure are the Fomblin Z series which are copolymers of tetrafluoroethylene oxide (C₂F₄O) and difluoromethylene oxide (CF₂O) as shown in the following equation:



Typically, the ratio of *x* to *y* in these fluids is 0.6 or 0.7 which would indicate approximately 1.5 (CF₂O) units for each (C₂F₄O) unit. In addition, these units are randomly distributed throughout the chain. The viscosity-temperature properties of these fluids appear in figure 5.

As can be seen, these fluids have excellent viscometric properties. Only the dimethyl silicones, with their highly flexible siloxane units, approach these low ASTM slopes.

None of the unbranched model compounds contained any difluoromethylene units. For comparison, perfluorodiglyme and perfluorotetraglyme appear in figure 5. These compounds contain only (C₂F₄O) units. Even taking into account their low MW, their slopes are still high. In fact, their slopes appear to fall on the reference curve for the branched fluids.

Also appearing in figure 5 is data for a series of commercial fluids produced by Daikin Industries (Demnum fluids). These fluids are unbranched and are based on the repeating unit (CF₂CF₂CF₂O). Therefore, one would expect their viscometric properties to be worse than the Fomblin Z series but better than the HFPO fluids. This is indeed the case. Perhaps a better comparison among the three series of fluids appears in figure 7. Here ASTM slope is plotted as a function of viscosity at 20 °C.

In summary, these data indicate that a fluid having the best viscometric properties (lowest ASTM slope) should possess the lowest C/O ratio in the polymer backbone and the lowest degree of branching. The ultimate fluid (for viscosity characteristics only) would then be a high MW perfluorinated polymer containing only difluoromethylene oxide units (CF₂O).

Oxidation Stability

Results for the oxidative degradation study appear in figure 3. Taking into account test reproducibility, the following order of oxidation stability was obtained: HFPO hexamer \cong perfluorotetraglyme > perfluoro(1,3 diethoxypropane) \cong perfluoro(1,4 diethoxybutane) > perfluoro(1,3 diethoxy-2,2 dimethylpropane) > perfluoro(pentaerythrityltetramethylether).

The two highly branched compounds yielded decomposition rates 4 to 6 times those of the most stable materials, the HFPO hexamer and perfluorotetraglyme. Both highly branched fluids contain quaternary carbons which may be a source for this instability. Branched structures will produce more stable free radicals thus favoring more rapid decomposition. There was no evidence of residual hydrogens, as measured by ¹⁹F nmr in any of the compounds. In

addition gas and liquid chromatographic analysis revealed purities in excess of 99 percent.

In contrast, the HFPO hexamer is very stable at these conditions and contains a branched trifluoromethyl group. It has been postulated that a single pendant group attached to a carbon atom adjacent to an oxygen in a PFAE may stabilize the polymer by sterically protecting the oxygen in the backbone of the polymer (ref. 18).

In summary, preliminary results indicate that the more highly branched PFAE fluids may be less oxidatively stable than fluids containing single trifluoromethyl groups or fluids containing no branching at all.

SUMMARY OF RESULTS

The results of viscosity-temperature and oxidative stability correlations with structures of perfluoroalkylether (PFAE) fluids are summarized as follows:

1. Increases in branching and size of the branching substituent caused a deterioration in viscometric properties (i.e., an increase in ASTM slope).
2. Increasing the ratio of carbon to oxygen also increased ASTM slope.
3. Preliminary oxidation stability tests indicated that highly branched PFAE fluids (containing quaternary carbons) may be less stable than either those containing a single pendant trifluoromethyl group or those containing no branching at all.

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TABLE I. - MODEL PERFLUOROPOLYETHER COMPOUNDS AND THE POLYMERS WHICH THEY MODEL

Model compounds		Boiling point, °C	Molecular weight	Polymers structure
Name	Structure			
Perfluorodiglyme	$\text{CF}_3(\text{OCF}_2\text{CF}_2)_2\text{OCF}_3$	65 to 66	386	$\text{CF}_3(\text{OCF}_2\text{CF}_2)_n\text{OCF}_3$
Perfluorotetraglyme	$\text{CF}_3(\text{OCF}_2\text{CF}_2)_4\text{OCF}_3$	138	618	
Perfluoro (1,3-diethoxypropane)	$\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$	75 to 76	420	$\text{CF}_3(\text{OCF}_2\text{CF}_2\text{CF}_2)_n\text{OCF}_3$
Perfluoro (1,4-diethoxybutane)	$\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_3$	96	470	$\text{CF}_3(\text{OCF}_2\text{CF}_2\text{CF}_2\text{CF}_2)_n\text{OCF}_3$
Hexafluoropropylene oxide ^a hexamer	$\text{CF}_3\text{CF}_2\text{CF}_2(\text{OCF}(\text{CF}_3)\text{CF}_2)_4\text{OCF}_2\text{CF}_3$	223	968	$\text{CF}_3(\text{OCF}(\text{CF}_3)\text{CF}_2)_n\text{OCF}_3$
Perfluoro(1,3-diethoxy- 2,2-dimethylpropane)	$\text{CF}_3\text{CF}_2\text{OCF}_2\text{C}(\text{CF}_3)_2\text{CF}_2\text{OCF}_2\text{CF}_3$	85	520	$\text{CF}_3(\text{OCF}_2\text{C}(\text{CF}_3)_2\text{CF}_2)_n\text{OCF}_3$
Perfluoro (Pentaerythrityltetramethyl ether)	$(\text{CF}_3\text{OCF}_2)_4\text{C}$	95	552	$\text{CF}_3(\text{OCF}_2\text{C}(\text{CF}_2\text{OCF}_3)_2\text{CF}_2)_n\text{OCF}_3$

^aNot synthesized, provided by Du Pont Co.

TABLE II. - VISCOSITY DATA

Compound	Kinematic viscosity, cS		ASTM slope
	38 °C (100 °F)	54 °C (130 °F)	
Perfluorodiglyme	0.345	0.287	1.08
Perfluorotetraglyme	.802	.631	1.01
Perfluoro(1,3-diethoxypropane)	.445	.344	1.43
Perfluoro(1,4-diethoxybutane)	.610	.440	1.61
HFPO hexamer	2.65	1.84	.95
Perfluoro(1,3-diethoxy- 2,2-dimethylpropane)	.707	.557	1.04
Perfluoro(pentaerythrityl- tetramethylether)	.711	.554	1.16

TABLE III. - THERMAL OXIDATIVE INVESTIGATION OF
PERFLUOROALKYLETERS

Compound (a)	Amount used, mg	Decomp. prod., mg	Decomp. rate percent/24 hr
Perfluorotetraglyme	163	0.4	0.12
HFPO hexamer	188	.4	.11
Perfluoro(1,3-diethoxypropane)	168	.7	.21
Perfluoro(1,4-diethoxybutane)	234	1.1	.24
Perfluoro(1,3-diethoxy- 2,2-dimethylpropane)	221	1.9	.43
Perfluoro(pentaerythrityl- tetramethylether)	195	2.5	.64

^a100 mm O₂ in each tube; test temperature, 360 °C; test duration, 48 hr.

- (1) PERFLUORODIGLYME
- (2) PERFLUOROTETRAGLYME
- (3) PERFLUORO (1, 3-DIETHOXYPROPANE)
- (4) PERFLUORO (1, 4-DIETHOXYBUTANE)
- (5) HFPO HEXAMER
- (6) PERFLUORO (1, 3-DIETHOXY-2, 2-DIMETHYLPROPANE)
- (7) PERFLUORO (PENTAERYTHRITYL TETRAMETHYL ETHER)

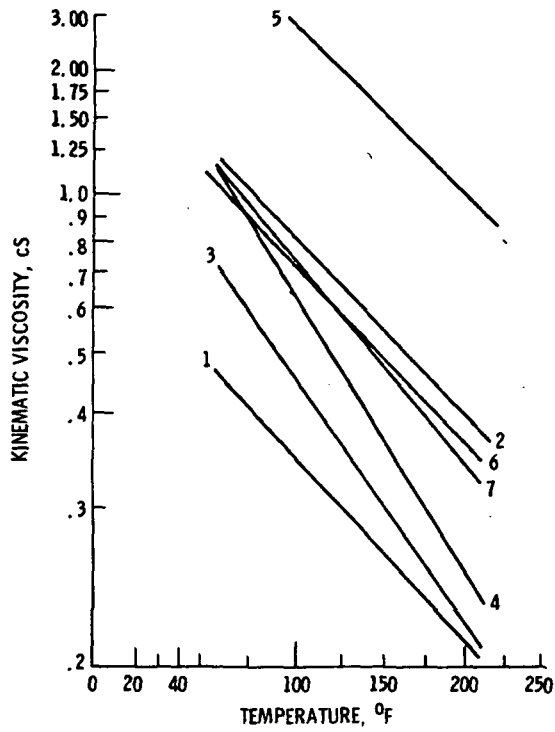


Figure 1. - Kinematic viscosity as a function of temperature for perfluoroalkylether compounds.

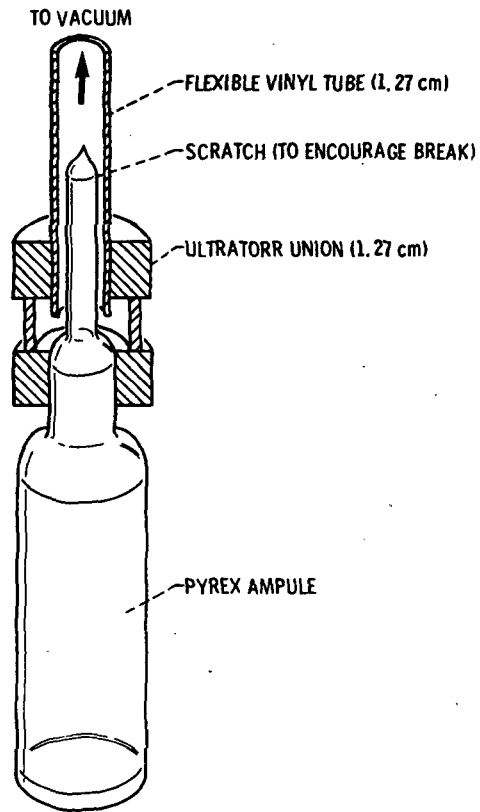


Figure 2. - High temperature degradation ampule.

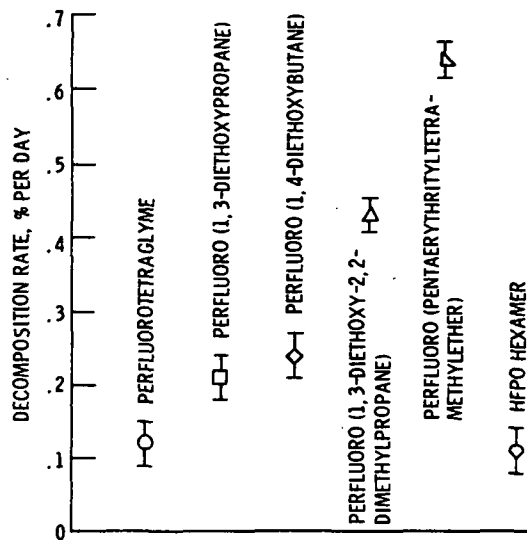


Figure 3. - Oxidative degradation of model perfluoroalkyethers. 360 °C, oxygen, 48 hr.

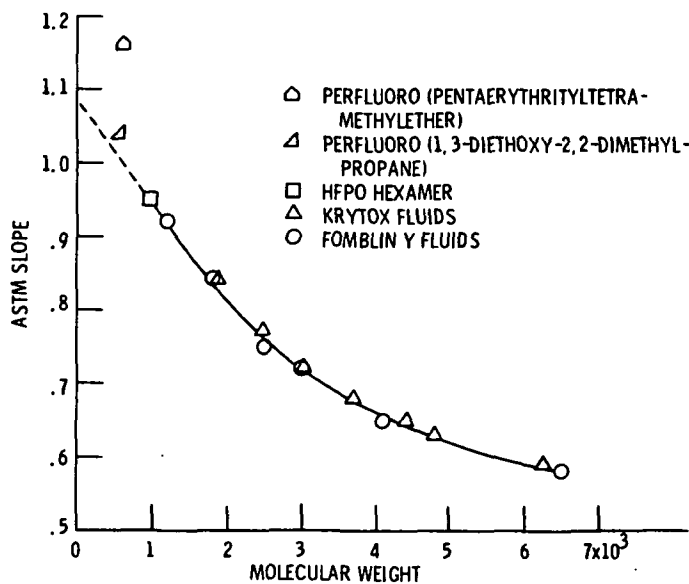


Figure 4. - Viscosity-temperature slope (ASTM) as a function of molecular weight for a series of branched perfluoroalkyethers.

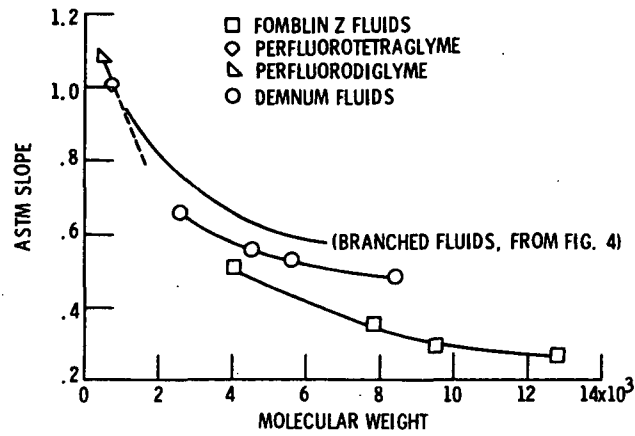


Figure 5. - Viscosity-temperature slope (ASTM) as a function of molecular weight for several unbranched perfluoroalkylethers.

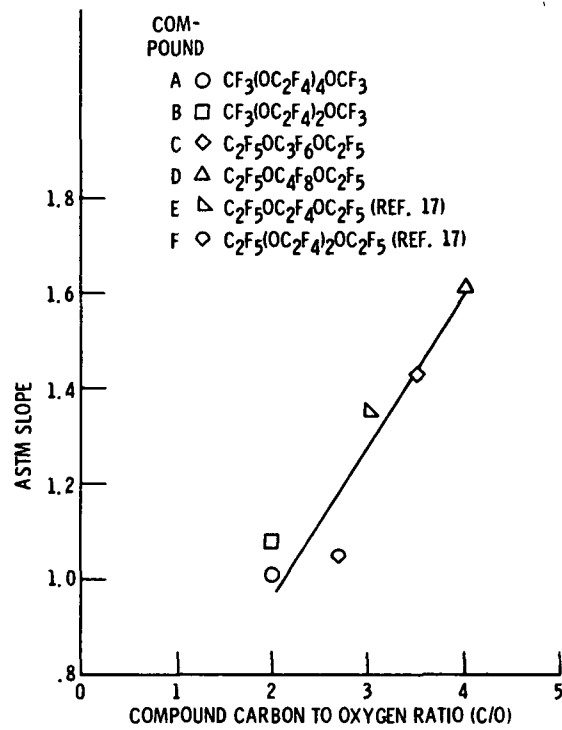


Figure 6. - Viscosity-temperature slope (ASTM) as a function of compound carbon to oxygen ratio (C/O) for a series of unbranched perfluoroalkylethers.

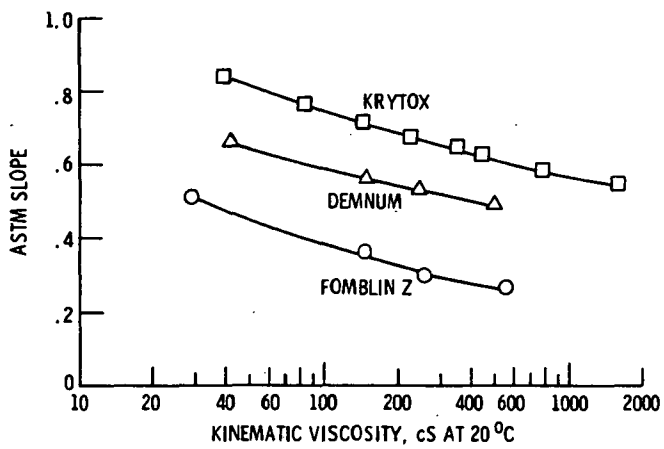


Figure 7. - Viscosity-temperature slope (ASTM) as a function of kinematic viscosity at 20 °C for Krytox, Demnum, and Fomblin Z fluids.

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16. Abstract A series of low molecular weight perfluoroalkylethers (PFAE) were synthesized by direct fluorination. Viscosity-temperature properties and oxidation stabilities were determined. Viscosity-temperature correlations indicated that increases in branching and increases in the size of the branching substituent caused a deterioration in viscometric properties (i.e., an increase in ASTM slope). In addition, increasing the ratio of carbon to oxygen in these compounds also increased the ASTM slope. Preliminary oxidation stability tests indicated that highly branched PFAE fluids (i.e., those containing quaternary carbons) may be less stable than either those containing a single trifluoromethyl pendant group or those containing no branching at all.					
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