Determination of the Thermal Stability of Perfluoroalkylethers

Larry S. Helmick and William R. Jones, Jr.
Lewis Research Center
Cleveland, Ohio

February 1990

NASA

DETERMINATION OF THE THERMAL STABILITY OF PERFLUOROALKYLETHERS

Larry S. Helmick* and William R. Jones, Jr.
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

The thermal decomposition temperatures of several commercial and custom synthesized perfluoroalkylether fluids were determined with a computerized tensimeter. In general, the decomposition temperatures of the commercial fluids were all similar and significantly higher than those for custom synthesized fluids. Correlation of the decomposition temperatures with the molecular structures of the primary components of the commercial fluids revealed that the stability of the fluids is not affected by intrinsic factors such as carbon chain length, branching, or cumulated difluoroformal groups. Instead, correlation with extrinsic factors revealed that the stability may be limited by the presence of small quantities of thermally unstable material and/or chlorine-containing material arising from the use of chlorine-containing solvents during synthesis. Finally, correlation of decomposition temperatures with molecular weights for Demnum and Krytox fluids supports a chain cleavage reaction mechanism for Demnum fluids and an unzipping reaction mechanism for Krytox fluids.

INTRODUCTION

Perfluoroalkylethers (PFAE) is a class of fluids which is presently being investigated for potential applications as high temperature engine lubricants (refs. 1 to 5). Several fluids, some commercially available and some custom synthesized, are now available for experimental evaluation. The commercial fluids are generally prepared by polymerization of perfluoromonomers (refs. 1 and 6 to 8). The custom synthesized fluids are prepared by direct fluorination of hydrogen-containing polymers (refs. 9 to 11).

An important property for high temperature engine applications is the thermal decomposition temperature. In the past, this property was determined with an isoteniscope technique (refs. 12 to 16). Recently a computerized tensimeter, based on the isoteniscope principle, has been developed (ref. 16) which automates many of the tedious procedures common to the isoteniscope technique. This tensimeter has now been used to determine the thermal decomposition temperatures of a variety of perfluoroalkylethers.

With an accurate and reproducible method for determining the thermal decomposition temperature, an attempt can now be made to understand the factors that determine this temperature. This understanding should allow the present upper temperature limits to be exceeded by designing and fabricating new fluids. There are two main areas, intrinsic and extrinsic, in which to seek this understanding. The first is in the intrinsic molecular structure of the molecule itself. Certain structures may be intrinsically more stable than others

---

due to higher bond strengths or molecular geometries which prevent decomposition by low energy of activation mechanisms. On the other hand, there may be extrinsic factors that limit the stability of a particular fluid. Such factors might be the presence of impurities such as hydrogen or chlorine in the molecule, or thermally unstable material in molecular form that catalytically degrades the fluid.

The purpose of this paper is to provide information on the stability of several PFAE fluids and to seek correlations with molecular structures, atomic and molecular impurity levels, and methods of preparation. It is anticipated that this type of correlation will eventually result in the design and synthesis of a fluid with good lubrication properties and maximum thermal stability.

EXPERIMENTAL

Materials

All PFAE fluids were tested as received. Names and chemical structures of the fluids are listed in tables I and II. Typical physical properties appear in tables III and IV. Data for commercial fluids were taken from company literature. No attempt was made to verify the data. Data for custom synthesized fluids are from references 10 and 11, or were determined by us. Symbols used in this report appear in the appendix.

Procedure

Thermal decomposition was performed in a borosilicate glass sample cell with the tensimeter (figs. 1 and 2) and test procedures previously described (ref. 16). For fluids containing small amounts of thermally unstable material, it was necessary to heat the fluid for 10 min at the expected decomposition temperature (± 10 °C) and degas the cell again in order to decompose most of the unstable material and minimize its interference. Thermal decomposition temperatures (T_d') and energies related to the energy of activation (E') were determined at a specific gas volume/heated liquid volume (V_g/V_l) ratio by plotting the log of the isothermal change in pressure during a 144 sec time interval (log dP/dt) versus the reciprocal absolute temperature (fig. 3). The thermal decomposition temperature (T_d) and the energy of activation (E) were then determined from a graph of $1/T_d'$ versus $\log V_g/V_l$ where $\log V_g/V_l = 0$ (fig. 4) and are reported in tables V to XI. Because of limited quantities, E was not determined for some fluids. For these fluids, T_d was determined directly at a $\log V_g/V_l$ ratio of zero. T_d's are considered to be accurate to ± 2 °C for fluids with values for E reported in the tables, and ± 4 °C for fluids with values for E'. E and E' are considered to be accurate to ± 17 kJ/mol.

Chlorine Analyses

Analyses for chlorine were determined with an x-ray fluorescence (XRF) technique (tables V to XI). A Phillips Model PW1410/80 x-ray spectrometer with a helium path, a 50 sec count time, and a graphite crystal angle (2θ) of 89.65° (chlorine K-α peak) was used. Standard deviations for all count rates were

2

less than 1 percent. Count rates are corrected for background at a crystal angle (2θ) of 91.50° by ratioing against a Krytox 143AB Lot 68 blank. The lower detection limit was 0.01 at %.

Hydrogen Analyses

Analyses for hydrogen were done on neat liquid samples with a Nicolet MX-1 FT-IR spectrometer using a 2.05 mm cell with sodium chloride windows. Hydrogen concentrations were read from a graph of absorbance versus concentration for a series of dilute standard solutions of Freon E fluids dissolved in HPLC grade 1,1,2-trichlorotrifluoroethane. The lower detection limit was 3 ppm.

RESULTS AND DISCUSSION

The thermal decomposition temperatures of the fluids tested seem to fall into two major groups: those above 628 K (355 °C) and those below. Temperatures above 628 K are generally exhibited by the commercial fluids, and those below by the custom synthesized fluids. The more thermally stable commercial fluids will be discussed first, followed by discussion of the custom synthesized fluids.

Demnum Fluids

The Demnum S and D fluids (table V) have consistently high thermal decomposition temperatures, ranging from 649.9 to 653.3 K (376.7 to 380.1 °C). The difference in T_d between the two lots of S-100 (0.5 °C) is less than the experimental error in measurement. Only traces of unstable material (pressure rises at temperatures < T_d) were detected.

The consistently high T_d and presence of only traces of unstable material may imply that the synthetic method for Demnum fluids, polymerization of tetrafluorooxetane followed by direct fluorination, is as good as any method presently being used to make PFAE fluids. Therefore, Demnum fluids provide a basis for comparing the T_d's of other fluids, produced by different procedures and with more complex molecular structures, in order to determine if the other synthetic methods or functional groups are detrimental to the thermal stability.

One Demnum fluid (C-240) containing 3 at % chlorine was analyzed as well (table V). The low T_d (301.0 °C) demonstrates that the presence of chlorine is detrimental to the stability of the molecule, probably due to the relatively weak carbon-chlorine bond. That the presence of a low concentration of a chlorine-containing substance with a decomposition temperature above 583 K (300 °C) does not introduce a second decomposition temperature, but can significantly reduce the T_d of a more stable fluid, is demonstrated by the sharp reduction in T_d for Demnum S-100 when 6 percent C-240 is added (table V). Addition of 25 percent C-240 reduced the T_d still further. The correspondingly low T_d of perfluoropoly(epichlorohydrin) (323.1 °C, table XI) compared with the T_d's of the Krytox fluids (355 to 376 °C, table VI), which have the same skeletal structure, also indicates that the presence of chlorine is detrimental to the thermal stability. Chlorine XRF analysis of both Demnum C-240 and perfluoropoly(epichlorohydrin) showed high count rates, as expected, due to the presence of chlorine.

3

Krytox Fluids

The T_d's (table VI) of the low molecular weight Krytox fluids 143AY, 649.2 K (376.0 °C), and 143AB, 644.2 K (371.0 °C), are nearly as high as those for the Demnum fluids. However, they appear to decrease by approximately 20 °C as the molecular weight (MW) of the fluid increases. A comparable decrease in T_d with increasing MW was not observed for any of the other fluids. This decrease is larger than the experimental error and therefore appears to be real.

Since all Krytox fluids have the same chemical structure, the decrease in T_d with increasing MW cannot be due to changes in the primary chemical structure. Furthermore, it cannot be attributed to an increasing concentration of residual hydrogen as the MW increases, since the T_d of "triply" fluorinated 143AD Lot 82, which has no detectable hydrogen at the 3 ppm sensitivity level, is no higher than the other lots of 143AD which contain measurable amounts of hydrogen. In addition, Freon E-11, which has the same structure as the Krytox fluids but contains one hydrogen in the end cap (514 ppm hydrogen), showed no significant thermal decomposition below 350 °C. (The T_d of 361.3 °C for Freon E-11 (table VI) has a larger than normal experimental error due to the fluid volatility. It also appears to be depressed by about 20 °C, presumably due to the presence of hydrogen, when compared to the T_d of 382 °C calculated for a Krytox fluid with the same MW (1946 g/mol) as Freon E-11.)

Effect of Molecular Weight

Finally, the following derivation of the relationship between MW and T_d indicates that a decrease in T_d, as determined by isothermal pressure increases, with increasing molecular weight, is probably due to the "unzipping" reaction mechanism for decomposition of Krytox fluids.

For the thermal decomposition reaction $B \rightarrow b\,D$, the rate constant (k) usually varies with temperature according to the Arrhenius rate law (ref. 13) as shown in equation (1).

$$k = Ae^{-E/RT} \tag{1}$$

where A is the frequency factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. Blake, et al. (ref. 13) have shown that the rate of isothermal pressure rise (dP/dt) due to formation of gaseous product (D) is also related to the rate constant by the gas volume/heated liquid volume ratio (V_g/V_ℓ) in the reaction cell, and the constants b, n_B^α, R, and T, as shown in equation (2).

$$k = \frac{V_g}{V_\ell \, b n_B^\alpha RT} \frac{dP}{dt} \tag{2}$$

where b is the number of molecules of gas D formed from one molecule of liquid B, n_B is the concentration of B, α is the order of the reaction, R is the gas constant, and T is the absolute temperature. Setting equations (1) and (2) equal to each other gives equation (3).

$$Ae^{-E/RT} = \frac{V_g}{V_\ell \, b \, n_B^\alpha RT} \frac{dP}{dt} \qquad (3)$$

Taking logs of equation (3) gives equation (4).

$$\log A - E/2.3RT = \log(V_g/V_\ell) + \log 1/b + \log 1/n_B^\alpha R + \log 1/T + \log dP/dt \qquad (4)$$

Solving equation (4) for $\log b$ results in equation (5).

$$\log b = E/2.3RT - \log A + \log V_g/V_\ell - \log n_B^\alpha R - \log T + \log dP/dt \qquad (5)$$

From the definition of the thermal decomposition temperature, we know that when $\log (V_g/V_1) = 0$ and $\log (dP/dt) = 0.30$, then $T = T_d$. Substituting these values into equation (5) produces equation (6).

$$\log b = E/2.3RT_d - \log A - \log n_B^\alpha R - \log T_d + 0.3 \qquad (6)$$

For decomposition of a series of fluids with increasing molecular weights but the same chemical structures and densities, such as Krytox fluids, $\log b$ and T_d will be variables while the other quantities are constant. Since $\log T_d$ is small and nearly constant (for small changes in T_d, ref. 16) compared with $E/2.3RT_d$, it can be included in the other constants. Therefore, under these experimental conditions, equation (6) reduces to equation (7).

$$\log b = E/2.3RT_d - \log C \qquad (7)$$

If the fluid decomposes by an "unzipping" reaction mechanism, then the number of molecules of gas formed from one molecule of liquid will be proportional to the molecular weight (MW) of the liquid (i.e., $b = k'MW$). Substituting this into equation (7) gives equation (8) which is the equation of a straight line.

$$\log MW = E/2.3RT_d - \log C' \qquad (8)$$

Theoretically, then, a plot of $\log MW$ versus $1/T_d$ should produce a straight line for a series of fluids with increasing molecular weight if they decompose by an unzipping reaction mechanism. This is the case experimentally, as shown in figure 5, for the Krytox fluids. Furthermore, the similarity in magnitude of the energy of activation (E) calculated from the slope of this graph (213 kJ/mol), to the values previously obtained (table VI), lend support to this interpretation of the data.

On the other hand, if the fluid decomposes by chain cleavage into two smaller fragments, then the number of molecules of gas formed from each reacting molecule (b) will not increase as the MW increases, but will remain constant, producing a constant T_d (eq. (7)). The Demnum fluids, which exhibit a constant T_d with increasing MW (table V), therefore appear to be decomposing by a chain cleavage mechanism. Sufficient data is not available for correlating decomposition temperatures with MW for the remaining fluids. Obviously,

care must be taken when comparing T_d's of high MW fluids decomposing by different mechanisms.

The absence of thermally unstable material, the high thermal stabilities of the lower MW Krytox fluids, and the reproducibility of thermal stability from one lot to another, as demonstrated by the decomposition temperatures of the six lots of 143AD, suggest that the synthetic method used in their preparation, polymerization of hexafluoropropylene oxide, is as good as that used for the Demnum fluids. Furthermore, since the lower MW Krytox fluids have T_d's which are similar to those for the Demnum fluids, it is apparent that neither the presence of the trifluoromethyl groups (branching) nor the tetrafluoroethylene groups (carbon chain length) in the Krytox structure has adversely affected the thermal stability.

Fomblin Z Fluids

The Fomblin Z fluids (table VII) exhibit T_d's which are similar to those for the Demnum fluids, but have a broader range. Reproducibility from lot to lot, as demonstrated by the two lots of Z-25, is good, which makes the broad range appear to be real. However, because only three different MW fluids could be analyzed, and because these fluids contained thermally unstable material which may be affecting the T_d slightly, it is uncertain whether there is any systematic change in T_d with MW.

The Fomblin Z fluids contain variable but significant amounts of material decomposing rapidly at 523 and 583 K (250 and 310 °C), well below the T_d of the major component of the fluid, as shown in figure 6. It was necessary to remove most of this unstable material by thermally stressing the fluid for 10 min at the expected T_d in order to minimize its interference with the determination of the T_d of the major component of the fluid. Detection of this material is significant because it demonstrates that thermal oxidative stability tests done at a constant temperature of 616 K (343 °C) (refs. 10 and 11) may be measuring only the concentration of this unstable material rather than the oxidative stability of the primary fluid.

Four Fomblin Z fluids were analyzed for chlorine by XRF. All four exhibited elevated count rates, indicating the presence of chlorine-containing material. Presumably the chlorine is being introduced during the polymerization process which involves a chlorine-containing solvent (ref. 17). Since Fomblin Z fluids also exhibit high thermal stability, the chlorine may be present in the thermally unstable material which is largely decomposed well before the T_d of the major component of the fluid is reached. However, XRF analysis of a thermally stressed sample of Z-15 P-9 indicated that no chlorine had been lost with the gaseous decomposition products.

In spite of the presence of chlorine-containing and thermally unstable materials, the high T_d's observed for the Fomblin Z fluids suggest that the method of synthesis, polymerization of tetrafluoroethylene in the presence of oxygen, is relatively good. The high T_d's also demonstrate that the random presence of difluoromethylene groups bonded to two oxygen atoms (difluoroformal groups), either as isolated or cumulated (in sequences) groups, does not reduce the thermal stability.

6

Fomblin Y Fluids

The Fomblin Y fluids are the only commercial fluids investigated which exhibit significantly reduced thermal stability compared to Demnum fluids. The T_d's of all of the Y fluids are well below 613 K (340 °C, table VII). The T_d range is about the same as for the Z fluids, and the two lots of Y-25 show good reproducibility. Like the Z fluids, they do not seem to show any systematic change in T_d with MW. In contrast to the Z fluids, none of the Y fluids contained detectable amounts of material with very low thermal stability, and no detectable amount of chlorine was present in the fluids analyzed by XRF (Y-25 S-20 and YR-1200 S-82).

What factor, then, is responsible for the reduced thermal stability of the Y fluids? The chemical structure of the Y fluids is similar to the Z fluids in that it contains random isolated and cumulated difluoroformal groups. However, this alone cannot be the cause of the reduced thermal stability of the Y fluids, since it did not reduce the stability of the Z fluids relative to the Demnum fluids. The structure is also similar to the Krytox fluids in that it contains a pendant trifluoromethyl group on a two carbon chain. But again, this is not likely to be the cause of the reduced thermal stability, since it did not reduce the stability of the low molecular weight Krytox fluids. Since neither chlorine-containing material nor material with low thermal stability was detected, it also cannot be attributed to either of these factors. However, the T_d's are approximately the same as those for the perfluoropoly-(dioxolane) #1 and perfluoropoly(trioxocane) #1 and #2 fluids (tables IX and X). Therefore, it is possible that some common factors are involved in reducing the stability of all of these fluids. Further investigation would be required to determine what these factors are and whether or not they are related to the molecular structures of the primary components, the presence of unstable material, or the methods of synthesis.

Perfluoropoly(ethylene Oxide)

The T_d's of perfluoropoly(ethylene oxide) fluids (table VIII) have as large a range as the Krytox fluids, but are about 15 °C lower. In this respect, they resemble Fomblin Y and the remaining custom synthesized fluids. The decreased thermal stability relative to Demnum, Krytox, and Fomblin Z fluids cannot be attributed to the tetrafluoroethylene group since the Fomblin Z fluids also contain the same group and exhibit high thermal stability. Furthermore, it cannot be attributed to the presence of significant amounts of hydrogen, since it contains less than 3 ppm residual hydrogen. However, the material appears to contain traces of chlorine. Consequently, the decreased thermal stability of this fluid may be related to the presence of chlorine-containing impurities.

Perfluoropoly(dioxolane)

Three lots of perfluoropoly(dioxolane) prepared by two different direct fluorination methods (refs. 10 and 11) were analyzed. The T_d's (table IX) are consistently low compared with the commercial fluids. The low T_d's cannot be attributed to the primary structure of the fluid, since Fomblin Z contains tetrafluoroethylene and isolated difluoroformal groups and is as stable as

7

Demnum. Furthermore, they cannot be attributed to the presence of significant amounts of hydrogen, since these fluids also contain less than 3 ppm hydrogen. Chlorine XRF analysis of dioxolane #1, which was prepared by a method which did not employ a chlorine-containing solvent, showed no significant chlorine. Analysis of dioxolane #2, however, which was synthesized by a method employing a chlorine-containing solvent, confirmed the presence of chlorine. Again, this may help to account for the low thermal stability of dioxolane #2, but some other factors must be affecting the T_d of dioxolane #1.

Perfluoropoly(trioxocane)

Three lots of perfluoropoly(trioxocane) prepared by different polymerization and direct fluorination methods (ref. 10) were analyzed. The T_d's (table X) are consistently lower than those for Demnum and Fomblin Z, although the high MW fraction of fluid #1 (bp > 370 °C) and #2 (bp > 350 °C) exhibit T_d's similar to the high MW Krytox fluids 143AD and 16256. The generally low thermal stability of these fluids again cannot be attributed to either the molecular structure of the primary component of the fluid or to the presence of residual hydrogen.

XRF analysis of fluids #1 and #2 detected no chlorine, which is consistent with the absence of chlorine-containing solvents in their synthesis. However, the synthetic method of fluid #3, which involved a chlorinated solvent, appears to have introduced chlorine-containing impurities in significant concentrations and may be responsible for the sharply reduced thermal stabilities for this fluid.

Two fractions (288 °C < bp < 350 °C, and bp > 350 °C) of fluid #3 also contain easily detectable amounts of material decomposing rapidly at 300 °C. Whether or not this material is similar to the low thermal stability material in the Fomblin Z fluids, and whether or not it is the chlorine-containing substance, has not been determined.

Miscellaneous PFAE Fluids

The thermal decomposition temperatures of the remaining PFAE fluids are similar to the custom synthesized fluids already discussed. They all exhibit reduced thermal stability (table XI) relative to the commercial fluids. This cannot be attributed to the molecular structure of the fluids, since all are very similar in structure to the three commercial fluids which are much more stable. Since all were made by direct fluorination procedures (ref. 11), it is again postulated that their relatively low thermal stabilities may be related to this synthetic method. None except perfluoropoly(epichlorohydrin) were analyzed for chlorine. Consequently, it has not been determined whether chlorine-containing material is responsible for their low thermal stabilities.

SUMMARY

The thermal decomposition temperatures of several commercially available as well as custom synthesized perfluoroalkylethers were determined with a computerized tensimeter. The decomposition temperatures of the commercial fluids

Demnum S and D, Krytox, and Fomblin Z were all similar and generally significantly higher than the decomposition temperatures of Fomblin Y and the custom synthesized fluids. Correlation of the decomposition temperatures with the chemical structures of the primary components of the fluids revealed that the thermal stability of the fluids is not affected by intrinsic factors such as carbon chain length, branching, or cumulated difluoroformal groups. Correlation of the decomposition temperatures with extrinsic factors suggested that the thermal stability of the fluids may be limited by the presence of thermally unstable material as well as chlorine-containing substances from chlorine-containing solvents used during synthesis. Finally, the results of correlating decomposition temperatures with molecular weights for Demnum and Krytox fluids are consistent with a chain cleavage mechanism for Demnum and an unzipping mechanism for Krytox. Therefore, care must be taken in comparing thermal decomposition temperatures (based on pressure measurements) for fluids degrading by different mechanisms.

CONCLUSIONS

The following conclusions can be drawn from thermal stability measurements of PFAE fluids using a tensimeter technique.

1. Small amounts of chlorine containing impurities introduced during synthesis can greatly reduce thermal decomposition temperatures of PFAE fluids.

2. PFAE fluids that thermally decompose by an unzipping mechanism rather than by cleavage will yield an apparently lower thermal decomposition temperature when measured by this technique.

3. The tensimeter technique provides a sensitive tool for measuring low levels (in the ppm range) of thermally unstable material in PFAE fluids.

APPENDIX

A   preexponential factor, s^{-1}

B   liquid reactant in a thermal decomposition

b   number of moles of product gas D

D   gaseous product from a thermal decomposition

E   energy of activation, kJ/mol

E'   energy related to E by the equation $E' = E + RT_m$ where R is the gas constant and T_m is the mean temperature for the range of observations (ref. 13), kJ/mol

k   rate constant for thermal decomposition, s^{-1}

n_B concentration of liquid reactant, g/L

P   pressure, torr

R   gas constant

T   absolute temperature, K

T_d thermal decomposition temperature at $V_g/V_l = 1$, K or °C

T_d' thermal decomposition temperature at $V_g/V_l \neq 1$, K or °C

t   time, sec

V_g gas volume, mL

V_l heated liquid volume, mL

α order of reaction

REFERENCES

1. Gumprecht, W.H.: PR-143 - A New Class of High-Temperature Fluids. ASLE Trans., vol. 9, no. 1, Jan. 1966, pp. 24-30.

2. Sianesi, D., et al.: Perfluoropolyethers: Their Physical Properties and Behaviour at High and Low Temperatures. Wear, vol. 18, 1971, pp. 85-100.

3. Snyder, C.E., Jr.; and Dolle, R.E., Jr.: Development of Polyperfluoro-alkylethers as High Temperature Lubricants and Hydraulic Fluids. ASLE Trans., vol. 19, no. 3, July 1976, pp. 171-180.

4. Snyder, C.E., Jr.; Gschwender, L.J.; and Tamborski, C.: Linear Polyper-fluoroalkylether-Based Wide-Liquid-Range High-Temperature Fluids and Lubri-cants. Lubr. Eng., vol. 37, no. 6, June 1981, pp. 344-349.

5. Jones, W.R., Jr.; and Snyder, C.E., Jr.: Boundary Lubrication, Thermal and Oxidation Stability of a Fluorinated Polyether and a Perfluoropolyether Triazine. ASLE Trans., vol. 23, no. 3, July 1980, pp. 253-261.

6. DuBoisson, R.A.; and Sellers, S.F.: Some Subtle But Significant Differ-ences Among Perfluoropolyether Vacuum Pump Fluids. Microelectronic Manu-facturing and Testing, Lake Publishing Co., Libertyville, IL, 1986.

7. Sianesi, D., et al.: Perfluoropolyethers by Photooxidation of Fluoro-olefins. Chim. Ind. (Milan), vol. 55, no. 2, 1973 pp. 208-221.

8. Ohsaka, Y.: Recent Advances in Synthetic Lubricating Oils. (8). Perfluo-rinated Polyethers. Petrotech (Tokyo), vol. 8, no. 9, 1985, pp. 840-843.

9. Jones, W.R., et al.: The Preparation of New Perfluoroether Fluids Exhibit-ing Excellent Thermal-Oxidative Stabilities. NASA TM-87284, 1986.

10. Bierschenk, T.R., et al: The Development of New, Low-Cost Perfluoroalkyl-ether Fluids with Excellent Low and High-Temperature Properties. NASA CR-182155, Exfluor Research Corp. Austin, TX, May 1988.

11. Bierschenk, T.R., et al.: The Preparation of New Perfluoropolyether Fluids Exhibiting Excellent Oxidative Stability. F33615-87-C-5307, Exfluor Research Corporation, Austin, TX, Apr. 22, 1988.

12. Fowler, L.; and Trump, W.N.: A Recording Tensimeter and Decomposition Tem-perature Detector. Analysis Instrumentation, Vol. 7, B.L. Connelly, L. Fowler, and R.G. Krueger, eds., ISA, 1969, pp. 141-144.

13. Blake, E.S., et al.: Thermal Stability as a Function of Chemical Struc-ture. J. Chem. Eng. Data, vol. 6, no. 1, Jan. 1961, pp. 87-98.

14. Jones, W.R., Jr.: Friction, Wear, and Thermal Stability Studies of Some Organotin and Organosilicon Compounds. NASA TN D-7175, 1973.

15. Vapor-Pressure-Temperature Relationship and Initial Decomposition Tempera-ture of Liquids by Isoteniscope. ASTM Standard D-2879-86, 1989.

16. Helmick, L.S.; and Jones, W.R., Jr.: Determination of the Thermal Stability of Perfluoroalkylethers by Tensimetry: Instrumentation and Procedure. NASA TM-102116, 1989. (Accepted for publication in STLE Tribol. Trans.)

17. Sianesi, D.; Pasetti, A.; and Belardinelli, G.: High Molecular Weight Perfluorinated Copolyethers from Tetrafluoroethylene. Federal Republic of Germany, Patent No. 2,238,094, Feb. 15, 1973.

TABLE I. – NAMES AND PRIMARY CHEMICAL STRUCTURES
OF COMMERCIAL PFAE FLUIDS

Name	Structure
Demnum S and D	$C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5$
Demnum C	$C_3F_7O(CFClCF_2CF_2O)_x(CF_2CF_2CF_2O)_yC_2F_5$
Krytox	$C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$
Fomblin Z	$CF_3O(CF_2CF_2O)_x(CF_2O)_yCF_3$
Fomblin Y	$C_3F_7O[CF(CF_3)CF_2O]_x(CF_2O)_yCF_3$
Freon E	$F[CF(CF_3)CF_2O]_xCHFCF_3$

TABLE II. – NAMES AND PRIMARY CHEMICAL STRUCTURES OF
CUSTOM SYNTHESIZED PFAE FLUIDS

Perfluoropoly–	Structure
(ethylene oxide)	$CF_3O(CF_2CF_2O)_xCF_3$
(dioxolane)	$CF_3O(CF_2CF_2OCF_2O)_xCF_3$
(trioxocane)	$CF_3O[(CF_2CF_2O)_2CF_2O]_xCF_3$
(tetrahydrofuran)	$CF_3O(CF_2CF_2CF_2CF_2O)_xCF_3$
(tetraethylene glycol/formaldehyde)	$CF_3O[(CF_2CF_2O)_4CF_2O]_xCF_3$
(dipropylene glycol/formaldehyde)	$CF_3O\{[CF(CF_3)CF_2O]_2CF_2O\}_xCF_3$
(1,2–epoxybutane)	$CF_3O[CF(CF_2CF_3)CF_2O]_xCF_3$
(epichlorohydrin)	$CF_3O[CF(CF_2Cl)CF_2O]_xCF_2CF_2Cl$

TABLE III. – PHYSICAL PROPERTIES OF
COMMERCIAL PFAE FLUIDS

Name	Average molecular weight, g/mol	Kinematic viscosity, cSt at 20 °C
Demnum		
S–65	4 500	150
S–100	5 600	250
S–200	8 400	500
D–700	14 000	600
C–240	6 500	630
Krytox		
143AY	3 000	150
143AB	3 700	230
143AX	4 800	450
143AC	6 250	800
143AD	8 250	1600
16256	11 000	------------
Fomblin		
Z–15	------------	148
Z–25	------------	250
Z–60	------------	------------
Y–25	3 000	250
Y–45	4 100	450
YR–1200	6 000 to 7 000	1000 to 2000
Freon		
E–11	1 946	------------

13

TABLE IV. – PHYSICAL PROPERTIES OF CUSTOM SYNTHESIZED PFAE FLUIDS

Perfluoropoly-	Boiling point range, °C at 0.05 torr[a]	Kinematic viscosity, cSt at 20 °C
(ethylene oxide)	245 to 288 288 to 343 >343	33.9 127 447
(dioxolane) #1	245 to 288 288 to 343 >343	23.0 50.8 238
(dioxolane) #2	245 to 288 >343	------ ------
(dioxolane) #3	200 to 300	24.4
(trioxocane) #1	288 to 370 >370	105 502
(trioxocane) #2	288 to 350 >350	83.3 291
(trioxocane) #3	245 to 288 288 to 350 >350	------ ------ ------
(tetrahydrofuran)	200 to 300	165
(tetraethylene glycol/formaldehyde)	>300	33.1
(dipropylene glycol/formaldehyde)	200 to 300 >300	72.2
(1,2-epoxybutane)	200 to 300	5688
(epichlorohydrin)	200 to 300	------

[a]Temperatures of 245 °C are at 10 torr.

TABLE V. – THERMAL DECOMPOSITION TEMPERATURES AND ENERGIES OF ACTIVATION FOR DEMNUM FLUIDS

[Listed in order of increasing molecular weight.]

Fluid	T_d, °C	E, kJ/mol	E', kJ/mol	Chlorine, at %
S-65	380.1	232	334	-----
S-100 Lot 1041	379.0	255	366	<0.01
S-100 Lot 2041	378.5	264	346	-----
S-200	376.7	245	308	<.01
D-700	379.3	230	351	-----
6 percent C-240 + 94 percent S-100	354.8	241	---	.18
25 percent C-240 + 75 percent S-100	341.9	237	---	-----
100 percent C-240	301.0	153	---	[a]3.0

[a]Calculated from formula.

TABLE VI. – THERMAL DECOMPOSITION TEMPERATURES
AND ENERGIES OF ACTIVATION FOR KRYTOX
AND FREON FLUIDS

[Krytox is listed in order of increasing molecular
weight.]

Fluid	T_d, °C	E, kJ/mol	E', kJ/mol	Chlorine, at %
Krytox				
143AY Lot 37	376.0	230	297	-----
143AB Lot 68	371.0	250	260	<0.01
143AX Lot 2	364.4	269	296	-----
143AC Lot 124	364.8	279	287	-----
143AD Lot 75	361.4	259	---	-----
143AD Lot 79	357.5	266	249	-----
143AD Lot 80	357.0	260	298	-----
143AD Lot 81	356.8	252	---	-----
143AD Lot 82	361.2	267	335	-----
a143AD Lot 82	359.6	254	---	-----
16256 Lot 6	355.2	256	269	<.01
Freon E-11	361.3	218	---	-----

a"Triply" fluorinated. No detectable hydrogen
remaining at 3 ppm level.

TABLE VII. – THERMAL DECOMPOSITION TEMPERATURES AND
ENERGIES OF ACTIVATION FOR FOMBLIN FLUIDS

[Listed in order of increasing molecular weight.]

Fluid	T_d, °C	E, kJ/mol	E', kJ/mol	Chlorine, at %
Z-15 P-9	383.9	292	251	0.01
Z-25 P-28	369.1	208	---	-----
Z-25 P-78	371.1	258	241	.09
Z-60 P-1	377.8	289	288	.09
Y-25 S-20	327.5	215	249	<.01
Y-25 S-133	328.2	209	---	-----
Y-45 S-17	334.0	228	---	-----
YR-1200 S-82	325.2	207	---	<.01

TABLE VIII. – THERMAL DECOMPOSITION TEMPERATURES
AND ENERGIES OF ACTIVATION FOR PERFLUOROPOLY-
(ETHYLENE OXIDE) FLUIDS

Fluid boiling point, °C	T_d, °C	E, kJ/mol	E', kJ/mol	Chlorine, at %
245 to 288	360.5	200	318	0.01
288 to 343	340.0	169	---	.01
>343	339.6	195	---	----

TABLE IX. – THERMAL DECOMPOSITION TEMPERA-
TURES AND ENERGIES OF ACTIVATION FOR
PERFLUOROPOLY(DIOXOLANE) FLUIDS

Fluid	Boiling point, °C	T_d, °C	E, kJ/mol	E', kJ/mol	Chlorine, at %
#1	245 to 288	334.5	198	---	-----
	288 to 343	333.0	210	---	-----
	>343	337.5	224	258	<0.01
#2	245 to 288	340.8	179	---	.02
	>343	337.3	203	276	-----
#3	200 to 300	326	190	---	-----

TABLE X. – THERMAL DECOMPOSITION TEMPERA-
TURES AND ENERGIES OF ACTIVATION FOR
PERFLUOROPOLY(TRIOXOCANE) FLUIDS

Fluid	Boiling point, °C	T_d, °C	E', kJ/mol	Chlorine, at %
#1	288 to 370	333.4	204	<0.01
	>370	358.1	267	<.01
#2	288 to 350	344.9	216	<.01
	>350	355.6	255	-----
#3	245 to 288	307.0	117	.10
	288 to 350	329.4	172	-----
	>350	329.3	178	.10

TABLE XI. – THERMAL DECOMPOSITION TEMPERATURES AND ENERGIES OF ACTIVATION
FOR MISCELLANEOUS PFAE FLUIDS

Perfluoropoly-	Boiling point, °C	T_d, °C	E', kJ/mol	Chlorine, at %
(tetrahydrofuran)	200 to 300	331.1	204	-----
(tetraethylene glycol/formaldehyde)	200 to 300	321.9	177	-----
(dipropylene glycol/formaldehyde)	200 to 300	335.5	219	-----
	>300	329.5	228	-----
(1,2-epoxybutane)	200 to 300	312.7	238	-----
(epichlorohydrin)	200 to 300	323.1	252	[a]10.0

[a]Calculated from molecular formula.
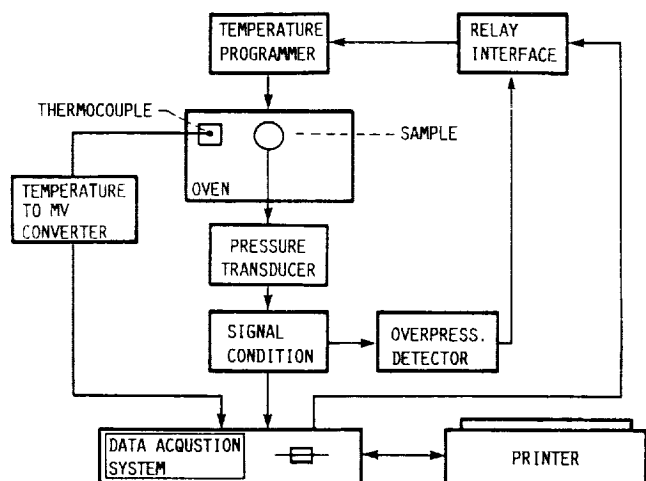
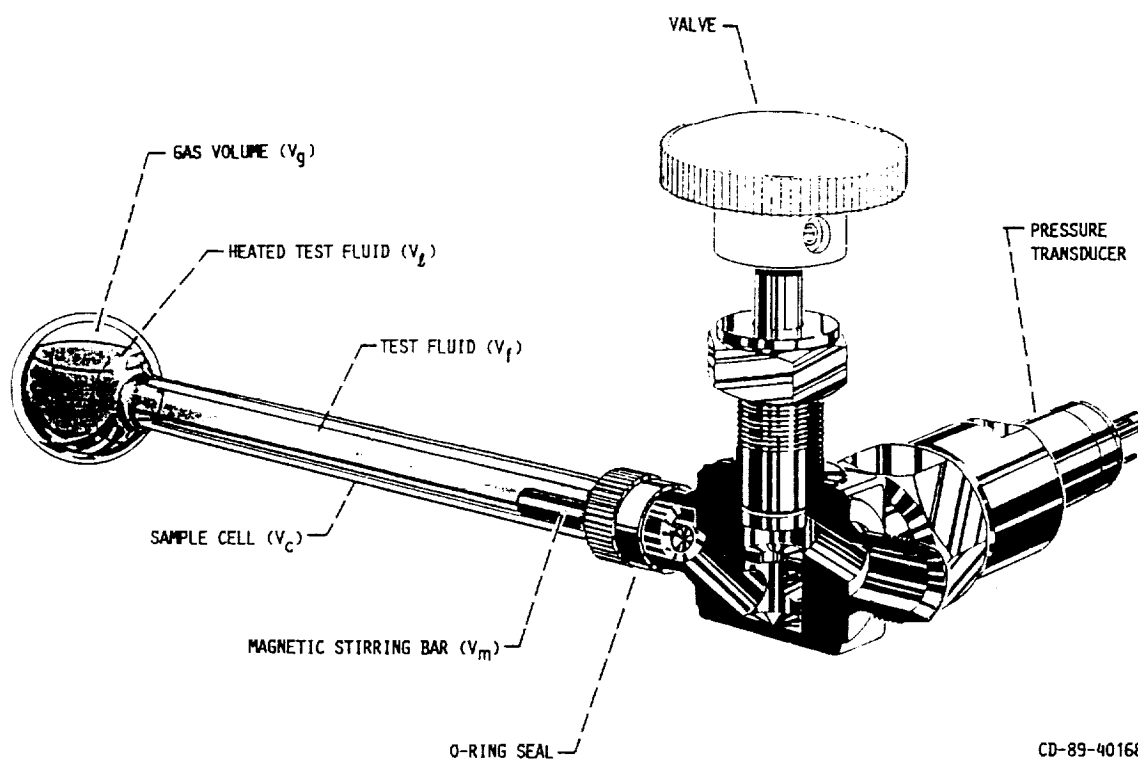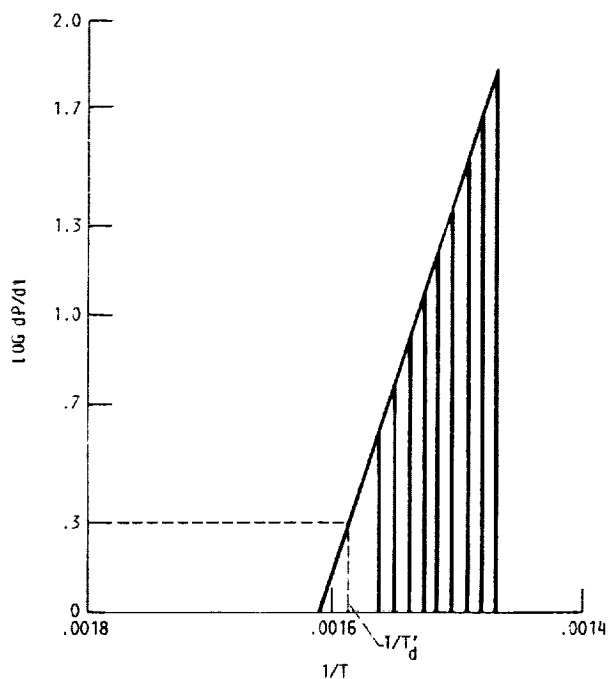FIGURE 1. - A SCHEMATIC DIAGRAM OF COMPUTERIZED TENSIMETER.

CD-89-40168

FIGURE 2. - CELL ASSEMBLY DURING TEST.

17

FIGURE 4. - DETERMINATION OF T_d FOR KRYTOX 16256. T_d = 355.2±2 ^oC (628.4 K); E = 269±9 kJ/MOL; COR. COEFF. - 0.994.

NUMBER	TEMPERATURE, ^oC	dP/dt	LOG, dP/dt	TOTAL P, TORR
1	365.0	4.338	0.6373	61.00
2	370.2	6.074	0.7834	79.22
3	375.1	7.809	0.8926	109.60
4	380.3	12.14	1.0845	152.98
5	385.1	15.61	1.1936	213.73
6	390.4	25.16	1.4007	303.97
7	395.6	34.70	1.5404	430.66
8	400.3	48.59	1.6865	612.02
9	405.5	72.02	1.8574	877.55

SLOPE = -13113.23

T_d' = 355.7 ^oC

E' = 251 kJ/MOL
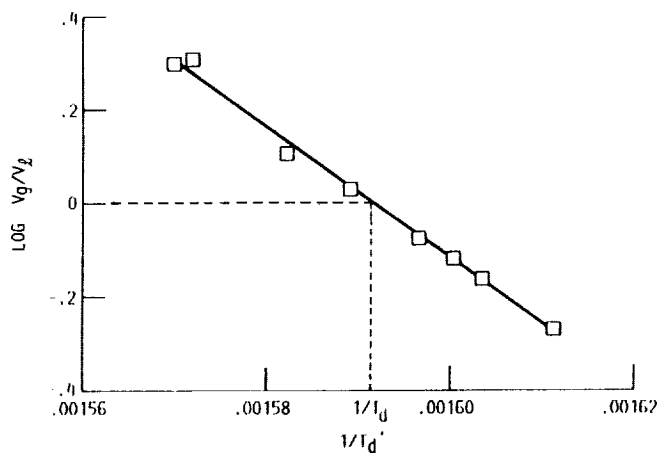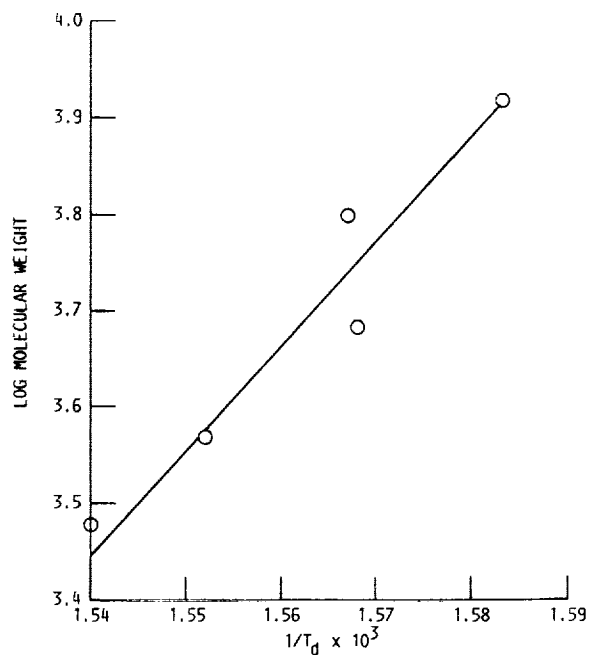
FIGURE 3. - DETERMINATION OF T_d' FOR KRYTOX 16256.

FIGURE 5. - DEPENDANCE OF T_d ON MOLECULAR WEIGHT FOR KRYTOX FLUIDS.
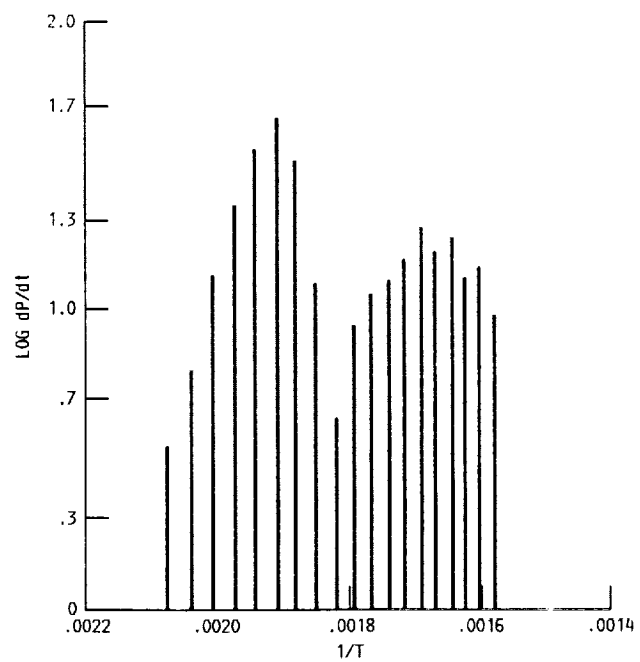
FIGURE 6. - THERMALLY UNSTABLE MATERIAL IN FOMBLIN Z-25 P67.

19

NASA
National Aeronautics and Space Administration

Report Documentation Page

1. Report No. NASA TM-102493	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

Determination of the Thermal Stability of Perfluoroalkylethers

5. Report Date

February 1990

6. Performing Organization Code

7. Author(s)

Larry S. Helmick and William R. Jones, Jr.

8. Performing Organization Report No.

E-5211

10. Work Unit No.

505-53-1A

9. Performing Organization Name and Address

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135-3191

11. Contract or Grant No.

13. Type of Report and Period Covered

Technical Memorandum

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

14. Sponsoring Agency Code

15. Supplementary Notes

Portions of this material were presented at the Japan International Tribology Conference sponsored by the Japan Society of Tribologists, Nagaya, Japan, October 29–November 1, 1990. Larry S. Helmick, National Research Council—NASA Research Associate at Lewis Research Center; on leave from Cedarville College, Cedarville, Ohio 45314. William R. Jones, Jr., NASA Lewis Research Center.

16. Abstract

The thermal decomposition temperatures of several commercial and custom synthesized perfluoroalkylether fluids were determined with a computerized tensimeter. In general, the decomposition temperatures of the commercial fluids were all similar and significantly higher than those for custom synthesized fluids. Correlation of the decomposition temperatures with the molecular structures of the primary components of the commercial fluids revealed that the stability of the fluids is not affected by intrinsic factors such as carbon chain length, branching, or cumulated difluoroformal groups. Instead, correlation with extrinsic factors revealed that the stability may be limited by the presence of small quantities of thermally unstable material and/or chlorine-containing material arising from the use of chlorine-containing solvents during synthesis. Finally, correlation of decomposition temperatures with molecular weights for Demnum and Krytox fluids supports a chain cleavage reaction mechanism for Demnum fluids and an unzipping reaction mechanism for Krytox fluids.

17. Key Words (Suggested by Author(s))

Perfluoroalkylethers
Liquid lubricants

18. Distribution Statement

Unclassified – Unlimited
Subject Category 27

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of pages 20	22. Price* A03