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DETERMINATION OF THE THERMAL STABILITY OF PERFLUOROPOLYALKYL ETHERS BY TENSIMETRY

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ABSTRACT

The thermal decomposition temperatures of several perfluoropolyalkyl ether 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 noncommercial 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 was not affected by carbon chain length, branching, or adjacent difluoroformal groups. Instead, stability was 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 two fluids supports a chain cleavage reaction mechanism for one and an unzipping reaction mechanism for the other.

INTRODUCTION

Perfluoropolyalkyl ethers (PFPAE) are presently being investigated for various applications in magnetic media, space mechanisms, high temperature engines, and hydraulic systems

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(Refs. 1-12). Several fluids are now available for experimental evaluation. The commercial fluids are generally prepared by polymerization of perfluoromonomers (Refs. 1, 13-15). The noncommercial fluids are prepared by direct fluorination of hydrogen-containing polymers (Refs. 16, 17).

An important property for high temperature applications in the absence of oxygen is the thermal decomposition temperature. In the past, this property was determined with an isoteniscope technique (Refs. 18-21). Recently a computerized tensimeter has been developed (Ref. 22) which automates many of the tedious procedures common to the isoteniscope technique.

With this accurate and reproducible method for determining thermal decomposition temperatures, 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 new fluids and new fluid treatments. There are two main areas in which to seek this understanding. The first is in the intrinsic molecular structure of the molecule itself. Certain structures may be more stable than others due to higher bond strengths or molecular geometries which prevent decomposition by low energy of activation mechanisms. The second involves extrinsic factors that may limit the stability of a particular fluid, such as hydrogen or chlorine in the molecule, or material that catalytically degrades the fluid.

The purpose of this paper is to provide information on the stability of several PFPAE 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 fluids with improved thermal stability.

EXPERIMENTAL

Materials

All PFPAE fluids were tested as received. Chemical structures of the fluids are shown 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 noncommercial fluids are from reference 10, or were determined by us. Symbols used in this report appear in the Appendix.

Sample cells were made from borosilicate glass tubing (Ref. 22), which is not necessarily inert. However, decomposition reactions using borosilicate cells containing borosilicate glass wool or quartz wool, as well as quartz cells containing quartz wool, showed no detectable change in results which could be attributed to the type of glass or the surface area. No experiments were conducted using metal cells or metal lined glass cells, although other work indicates that metal oxide surfaces can exhibit catalytic effects (Refs. 8, 10, 25).

Procedure

Thermal decomposition was performed with the tensimeter (Figures 1 and 2) and test procedures previously described (Refs. 22, 24). 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 second time interval (log dP/dt) versus the reciprocal absolute temperature (Figure 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 $V_g/V_l = 0$ (Figure 4) and are reported in Tables V-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 commercial 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 less than 1%. Count rates are corrected for background at a crystal angle (2θ) of 91.50° by ratioing against a K-2 blank.

Hydrogen Analyses

Analyses for hydrogen were done on neat liquid samples with a commercial FT-IR spectrometer using a 2.05 mm cell with sodium chloride windows. The basis for this analysis is the C-H stretching frequency at 2999 cm^{-1}. Hydrogen concentrations were read from a graph of absorbance vs concentration for a series of dilute standard solutions of 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 fell into two 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 noncommercial fluids. The more thermally stable commercial fluids will be discussed first, followed by discussion of the noncommercial fluids.

D Fluids

The DS and DD fluids (Table V) have consistently high thermal decomposition temperatures, ranging from 649.9 K (376.7°C) to 653.3 K (380.1°C). The difference in T_d between the two lots of DS-1 (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 implies that the synthetic method for D fluids, polymerization of tetrafluorooxetane followed by direct fluorination, is as good as any method presently being used to make PFPAE fluids. Therefore, D 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 D fluid (DC) containing 3 atom percent chlorine was analyzed as well (Table V). The low T_d (301.0°C) demonstrates that the presence of chlorine in the polymer backbone is detrimental to the stability of the molecule, probably due to the relatively weak carbon-chlorine bond. The fact 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 DS-1 when 6% DC is added (Table V). Addition of 25% DC 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 K fluids (355-376°C, Table VI), which have the same skeletal structure, indicates that the presence of chlorine in the pendant methyl substituent is also detrimental, but less so than chlorine residing in the backbone. Chlorine XRF analysis of both DC and perfluoropoly(epichlorohydrin) showed high count rates, as expected, due to the presence of chlorine.

K Fluids

The T_d's (Table VI) of the low molecular weight (MW) K fluids K-1, 649.2 K (376.0°C) and K-2, 644.2 K (371.0°C), are nearly as high as those for the D fluids. However, they decrease by approximately 20°C as the MW of the fluid increases. A comparable decrease in T_d with increasing MW was not observed for any of the other fluids, with the possible exception of the perfluoropoly(ethylene oxide) fluids. This decrease is larger than the experimental error and therefore is real.

Since all K 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 K-5 Lot 5, which has no detectable hydrogen (FT-IR) at the 3 ppm sensitivity level, is no higher than the other lots of K-5 which contain measurable amounts of hydrogen (>3 ppm). In addition, fluid E, which has the same structure as the K fluids but contains one hydrogen in the end cap (514 ppm hydrogen), showed no significant thermal decomposition below 350°C.

For thermal decomposition of a series of fluids with increasing molecular weights but the same chemical structures, densities, and molecular weight distributions, by an "unzipping" reaction mechanism, it has been shown (Ref. 24) that the relationship between MW and T_d is:

$$\log MW = E/2.3RT_d - \log C$$

where E is the energy of activation, R is the gas constant, and C is a constant.

Theoretically, then, a plot of log MW vs $1/T_d$ 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 for the K fluids, as shown in figure 5. 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 (i.e., an unzipping mechanism).

On the other hand, if the fluid decomposes by chain cleavage, the T_d will not decrease as the MW increases, but should remain constant or increase. The D fluids, which exhibit essentially a constant T_d with increasing MW (Table V), therefore appear to be decomposing by a chain cleavage mechanism. Sufficient data are not available for correlating decomposition temperatures with MW for the remaining fluid. In addition, no conclusions could be drawn concerning possible effects of the terminal groups on the thermal decomposition reaction mechanism for the K fluids. Obviously, care must be taken when drawing conclusions from T_d's of high MW fluids which may be decomposing by different mechanisms.

The absence of thermally unstable impurities, the high thermal stabilities of the lower MW K fluids, and the repeatability of thermal stability from one lot to another, as demonstrated by the decomposition temperatures of the six lots of K-5, suggest that the synthetic method used in their preparation, polymerization of hexafluoropropylene oxide, is as good as that used for the D fluids. Furthermore, since the lower MW K fluids have T_d's which are similar to those for the D fluids, it is apparent that neither the presence of the trifluoromethyl groups (branching) nor the tetrafluoroethylene groups (carbon chain length) in the K structure has adversely affected the thermal stability. (Although branching introduces steric hindrance, and therefore could conceivably reduce the thermal stability, it does not appear to be large enough to be detectable in the K fluids.)

Z Fluids

The Z fluids (Table VII) exhibit T_d's which are similar to those for the D fluids, but have a broader range. Repeatability from lot to lot, as demonstrated by the two lots of Z-2, 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, it is uncertain whether there is any systematic change in T_d with MW.

The Z fluids contain variable but significant amounts of material decomposing rapidly at 523 K (250°C) and 583 K (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 and degassing again 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) (Ref. 17) may be measuring only the concentration of this unstable material rather than the oxidative stability of the primary fluid.

Four 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. 23).

In spite of the presence of chlorine-containing and thermally unstable materials, the high T_d's observed for the 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 adjacent groups, does not greatly reduce the thermal stability.

Y Fluids

The Y fluids are the only commercial fluids investigated which exhibit significantly reduced thermal stability compared to D 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-1 show good repeatability. 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-1 Lot 1 and Y-3).

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 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 D fluids. The structure is also similar to the K 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 K fluids. Since neither chlorine-containing material nor material with low thermal stability was detected, it also cannot be attributed to either of these factors.

Perfluoropoly(ethylene Oxide)

The T_d's of perfluoropoly(ethylene oxide) fluids (Table VIII) have as large a range as the K fluids, but are about 15°C lower. In this respect, they resemble fluid Y and the remaining noncommercial fluids. The decreased thermal stability relative to the D, K, and Z fluids cannot be attributed to the tetrafluoroethylene group since the Z fluids also contain the same group and exhibit higher thermal stability. Furthermore, it cannot be attributed to the presence of significant amounts of hydrogen, since these fluids contain less than 3 ppm residual hydrogen. However, the material does 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 (Ref. 10) 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 fluid Z contains tetrafluoroethylene and isolated difluoroformal groups and is as stable as fluid D. 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 detectable 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 fluids D and 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 K fluids K-5 and K-6. 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, has introduced chlorine-containing impurities in significant concentrations and may be responsible for the 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. The origin of this material has not been determined.

Miscellaneous PFPAE Fluids

The thermal decomposition temperatures of the remaining PFPAE fluids are similar to the noncommercial fluids already discussed. They all exhibit reduced thermal stability (Table XI) relative to the commercial fluids. This cannot be attributed to the primary molecular structure of the fluids, since all are very similar to the three commercial fluids which are much more stable. Since all were made by direct fluorination procedures (Ref. 17), 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 perfluoropolyalkyl ethers were determined with a computerized tensimeter. The decomposition temperatures of the commercial fluids DS, DD, K, and Z were all similar and generally significantly higher than the decomposition temperatures of Y and the noncommercial 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 adjacent difluoroformal groups. However, it does appear to be affected 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 D and K fluids are consistent with a chain cleavage mechanism for D and an unzipping mechanism for K.

CONCLUSIONS

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

1. Thermal stability of presently available PFPAE fluids is not affected by carbon chain length, branching, or adjacent difluoroformal groups.

2. Thermal stability may be limited by the presence of small amounts of thermally unstable and/or chlorine containing impurities introduced during synthesis.

3. PFPAE fluids that thermally decompose by an unzipping mechanism rather than by cleavage will yield an apparently lower thermal decomposition temperature when measured by the tensimeter technique.

4. The tensimeter technique provides a sensitive tool for measuring low levels (in the ppm range) of thermally unstable material in PFPAE fluids and therefore is an excellent quality control device.

APPENDIX

Symbol	Units	Definition
E	kJ/mol	Energy of activation
E'	kJ/mol	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. 19).
P	torr	Pressure
R		Gas constant
T_d	K or °C	Thermal decomposition temperature at $V_g/V_l = 1$
T_d'	K or °C	Thermal decomposition temperature at V_g/V_l not equal to 1
T	K	Absolute temperature
t	s	Time
V_g	mL	Gas volume
V_l	mL	Heated liquid volume

REFERENCES

(1) Gumprecht, W.H., "PR-143 - A New Class of High-Temperature Fluids," ASLE Trans., 9, pp 24-30 (1966).

(2) Sianesi, D., Zamboni, V., Fontanelli, R., and Binaghi, M., "Perfluoropolyethers. Their Physical Properties and Behavior at High and Low Temperatures," Wear, 18, pp 85-100 (1971).

(3) Snyder, C.E., Jr., and Dolle, R.E., "Development of Polyperfluoroalkylethers as High Temperature Lubricants and Hydraulic Fluids," ASLE Trans., 19, pp 171-180 (1976).

(4) Snyder, C.E., Jr., Gschwender, L.J., and Tamborski, C., "Linear Polyperfluoroalkylether-Based Wide-liquid-Range High-Temperature Fluids and Lubricants," Lubr. Eng., 37, pp 344-349 (1981).

(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., 23, pp 253-261 (1980).

(6) Carre, D.J., "Perfluoropolyalkylether Oil Degradation: Inference of FeF_3 Formation on Steel Surfaces under Boundary Conditions," ASLE Trans., 29, pp 121-125 (1986).

(7) Skryabina, T.G., Nikonorov, E.M., Petrova, L.N., and Kobzova, R.I., "Termicheckij Analiz Perftorpoliehfirov i Smazok Na Ikh Osnove," Khim. Tekhnol. Topl. Masel, 7, pp 33-34 (1988). "Thermal Analysis of Perfluorinated Polyethers and Lubricants Based on Them," NASA TT-21138, (1992).

(8) Basu, P., Ballinger, T.H., and Yates, J.T., Jr., "Fluoroalkyl Ether Chemistry on Alumina: A Transmission Infrared Study of the Adsorption and Thermal Decomposition of $(CF_2H)_2O$ on Al_2O_3," Langmuir, 5, pp 502-510 (1989).

(9) Pacansky, J., Miller, M., Hatton, W., Liu, B., and Scheiner, A., "Study of the Structure of Perfluoro Ethers: Structural Models for Poly(perfluoroformaldehyde), Poly(perfluoroethylene oxide), and Poly(perfluoropropylene oxide)," J. Am. Chem. Soc., 113, pp 329-343 (1991).

(10) Kasai, P.H., Tang, W.T., and Wheeler, P., "Degradation of Perfluoropolyethers catalyzed by Aluminum Oxide," Appl. Surf. Sci., 51, pp 201-211 (1991).

(11) Vurens, G., Zehringer, R., and Saperstein, D., "The Decomposition Mechanism of Perfluoropolyether Lubricants during Wear," Surface Science Investigations in Tribology, American Chemical Society, pp 169-180 (1992).

(12) Fusaro, R.L., "Lubricaton of Space Systems—Challenges and Potential Solutions," NASA TM-105560, Lewis Research Center, Cleveland, OH (1992).

(13) DuBoisson, R.A., and Sellers, S.F., "Some Subtle But Significant Differences Among Perfluoropolyether Vacuum Pump Fluids," Microelectronic Manufacturing and Testing, July 1986.

(14) Sianesi, D., Pasetti, A., Fontanelli, R., and Bernardi, G.C., "Perfluoropolyethers by Photooxidation of Fluoroolefins," Chim. Ind. (Milan), 55, pp 208-221 (1973).

(15) Ohsaka, Y., "Recent Advances in Synthetic Lubricating Oils. (8). Perfluorinated Polyethers," Petrotech (Tokyo), 8, pp 840-843 (1985).

(16) Jones, W.R., Jr., Bierschenk, T.R., Juhlke, T.J., Kawa, H., and Lagow, R.J., "The Preparation of New Perfluoroether Fluids Exhibiting Excellent Thermal-Oxidative Stabilities," NASA TM-87284, Lewis Research Center, Cleveland, OH (1986).

(17) Bierschenk, T.R., Kawa, H., Juhlke, T.J., and Lagow, R.J., "The Development of New, Low-cost Perfluoroalkylether Fluids with Excellent Low and High-Temperature Properties," NASA CR182155, Exfluor Research Corporation, Austin, TX (1988).

(18) Fowler, L., and Trump, W.N., "A Recording Tensimeter and Decomposition Temperature Detector," Analysis Instrumentation, Vol. 7, B. Connelly, L. Fowler, and R. Krueger, eds., ISA, pp 141-144 (1969).

(19) Blake, E.S., Hammann, W.C., Edwards, J.W., Reichard, T.E., and Ort, M.R., "Thermal Stability as a Function of Chemical Structure," J. Chem. Eng. Data, 6, pp 87-98 (1961).

(20) Jones, W.R., Jr., "Friction, Wear, and Thermal Stability Studies of Some Organotin and Organosilicon Compounds," NASA TN D-7175, Lewis Research Center, Cleveland, OH (1973).

(21) "Vapor-Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope," ASTM Standard D-2879-86, (1989).

(22) Helmick, L.S., and Jones, W.R., Jr., "Determination of the Thermal Stability of Fluids by Tensimetry: Instrumentation and Procedure," Tribol. Trans. 33, pp 519-528 (1990).

(23) 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.

(24) Helmick, L.S., and Jones, W.R., Jr., "Determination of the Thermal Stability of Perfluoroalkylethers," NASA TM-102493, Lewis Research Center, Cleveland, OH (1990).

(25) Morales, W., "Surface Catalytic Degradation Study of Two Linear Perfluoropolyalkylethers at 345° C," NASA Technical Paper 2774, Lewis Research Center, Cleveland, OH, (1987).

TABLE I

Primary Chemical Structures of Commercial PFPAE Fluids

FLUID	STRUCTURE
DS and DD	$C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5$
DC	$C_3F_7O(CFClCF_2CF_2O)_x(CF_2CF_2CF_2O)_yC_2F_5$
K	$C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$
Z	$CF_3O(CF_2CF_2O)_x(CF_2O)_yCF_3$
Y	$C_3F_7O[CF(CF_3)CF_2O]_x(CF_2O)_yCF_3$
E	$F[CF(CF_3)CF_2O]_xCHFCF_3$

TABLE II

Primary Chemical Structures of Noncommercial PFPAE Fluids

NAME: 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)	$CF_3O(CF_2CF_2CF_2CF_2O)_xCF_2CF_2CF_3$
(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)	$CF_3O[CF(CF_2CF_3)CF_2O]_xCF_2CF_2CF_3$
(epichlorohydrin)	$CF_3O[CF(CF_2Cl)CF_2O]_xCF_2CF_2Cl$

TABLE III

Physical Properties of Commercial PFPAE Fluids

FLUID	AVERAGE MOLECULAR WEIGHT (g/mol)	KINEMATIC VISCOSITY mm^2/s (cSt) @ 20°C
DS-0	4500	150
DS-1	5600	250
DS-2	8400	500
DD	14000	600
DC	6500	630
K-1	3000	150
K-2	3700	230
K-3	4800	450
K-4	6250	800
K-5	8250	1600
K-6	11000	2717
Z-1	8000	148
Z-2	9500	250
Z-3	13000	560
Y-1	3000	250
Y-2	4100	450
Y-3	6,000-7,000	1000-2000
E	1946	

TABLE IV

Physical Properties of Noncommercial PFPAE Fluids

NAME Perfluoropoly-	BP RANGE (°C @ 0.05 Torr)*	KINEMATIC VISCOSITY mm^2/s (cSt) @ 20°C
(ethylene oxide)	245-288	33.9
	288-343	127
	>343	447
(dioxolane) #1	245-288	23.0
	288-343	50.8
	>343	238
(dioxolane) #2	245-288	-
	>343	-
(dioxolane) #3	200-300	24.4
(trioxocane) #1	288-370	105
	>370	502
(trioxocane) #2	288-350	83.3
	>350	291
(trioxocane) #3	245-288	-
	288-350	-
	>350	-
(tetrahydrofuran)	200-300	165
(tetraethylene glycol/formaldehyde)	>300	33.1
(dipropylene glycol/formaldehyde)	200-300	72.2
	>300	-
(1,2-epoxybutane)	200-300	5688
(epichlorohydrin)	200-300	-

* Temperatures of 245°C are at 10 Torr.

TABLE V

Thermal Decomposition Temperatures and Energies of Activation for D Fluids*

FLUID	T_d (°C)	E′ (kJ/mol)	E*** (kJ/mol)	CHLORINE (Atom %)
DS-0	380.1	232	334	-
DS-1 Lot 1	379.0	255	366	<0.01
DS-1 Lot 2	378.5	264	346	-
DS-2	376.7	245	308	<0.01
DD	379.3	230	351	-
6% DC + 94% DS-1	354.8	241	-	0.18
25% DC + 75% DS-1	341.9	237	-	0.75**
100% DC	301.0	153	-	3.0**

* Listed in order of increasing molecular weight.

** Calculated from formula.

*** See procedure.

TABLE VI

Thermal Decomposition Temperatures and Energies of Activation for K* and E Fluids

FLUID	T_d (°C)	E′ (kJ/mol)	E*** (kJ/mol)	CHLORINE (Atom %)
K-1	376.0	230	297	-
K-2	371.0	250	260	<0.01
K-3	364.4	269	296	-
K-4	364.8	279	287	-
K-5 Lot 1	361.4	259	-	-
K-5 Lot 2	357.5	266	249	-
K-5 Lot 3	357.0	260	298	-
K-5 Lot 4	356.8	252	-	-
K-5 Lot 5	361.2	267	335	-
K-5 Lot 5**	359.6	254	-	-
K-6	355.2	256	269	<0.01
E	361.3	218	-	-

* Listed in order of increasing molecular weight.

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

*** See procedure.

TABLE VII

Thermal Decomposition Temperatures and Energies of Activation for Z and Y Fluids*

FLUID	T_d (°C)	E′ (kJ/mol)	E** (kJ/mol)	CHLORINE (Atom %)
Z-1	383.9	292	251	0.10
Z-2 Lot 1	369.1	208	-	-
Z-2 Lot 2	371.1	258	241	0.09
Z-3	377.8	289	288	0.09
Y-1 Lot 1	327.5	215	249	<0.01
Y-1 Lot 2	328.2	209	-	-
Y-2	334.0	228	-	-
Y-3	325.2	207	-	<0.01

* Listed in order of increasing molecular weight.

** See procedure.

TABLE VIII

Thermal Decomposition Temperatures and Energies of Activation for Perfluoropoly(ethylene oxide) Fluids

FLUID b.p. (°C)	T_d (°C)	E′ (kJ/mol)	E* (kJ/mol)	CHLORINE (Atom %)
245-288	360.5	200	318	0.01
288-343	340.0	169	-	0.01
>343	339.6	195	-	-

* See procedure.

TABLE IX

Thermal Decomposition Temperatures and Energies of Activation for Perfluoropoly(dioxolane) Fluids

FLUID	b.p.** (°C)	T_d (°C)	E′ (kJ/mol)	E* (kJ/mol)	CHLORINE (Atom %)
#1	245-288	334.5	198	-	-
	288-343	333.0	210	-	-
	>343	337.5	224	258	<0.01
#2	245-288	340.8	179	-	0.02
	>343	337.3	203	276	-
#3	200-300	326	190	-	-

* See procedure.
**At reduced pressure.

TABLE X

Thermal Decomposition Temperatures and Energies of Activation for Perfluoropoly(trioxocane) Fluids

FLUID	b.p.* (°C)	T_d (°C)	E′ (kJ/mol)	CHLORINE (Atom %)
#1	288-370	333.4	204	<0.01
	>370	358.1	267	<0.01
#2	288-350	344.9	216	<0.01
	>350	355.6	255	-
#3	245-288	307.0	117	0.10
	288-350	329.4	172	-
	>350	329.3	178	0.10

*At reduced pressure.

TABLE XI

Thermal Decomposition Temperatures and Energies of Activation for Miscellaneous PFPAE Fluids

FLUID: Perfluoropoly-	b.p.** (°C)	T_d (°C)	E′ (kJ/mol)	CHLORINE (Atom %)
(tetrahydrofuran)	200-300	331.1	204	-
(tetraethylene glycol/formaldehyde)	200-300	321.9	177	-
(dipropylene glycol/formaldehyde)	200-300	335.5	219	-
	>300	329.5	228	-
(1,2-epoxybutane)	200-300	312.7	238	-
(epichlorohydrin)	200-300	323.1	252	10.0*

*Calculated from molecular formula.
**At reduced pressure.

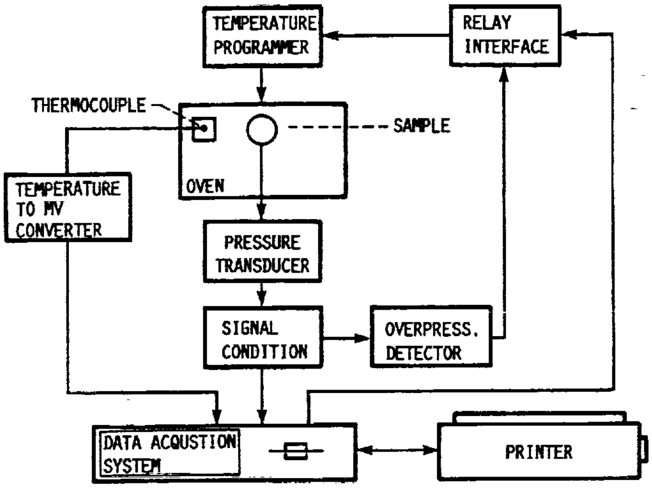


Figure 1.—A schematic diagram of computerized tensimeter.

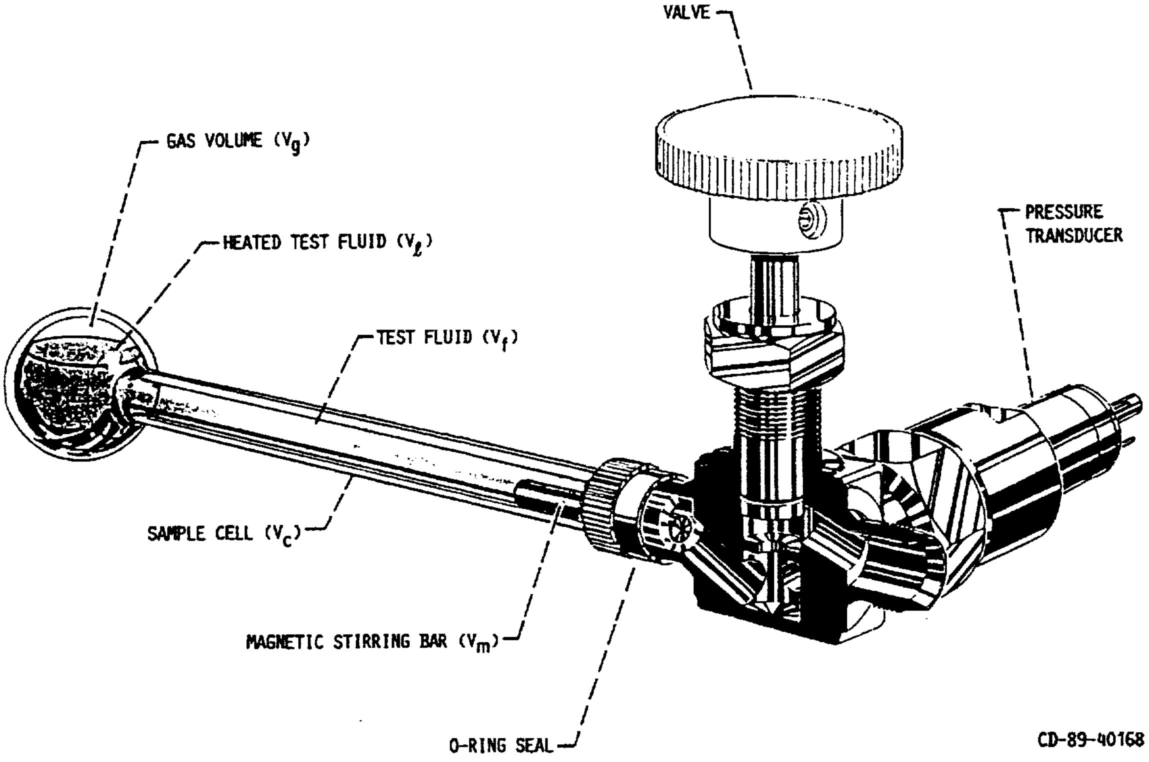
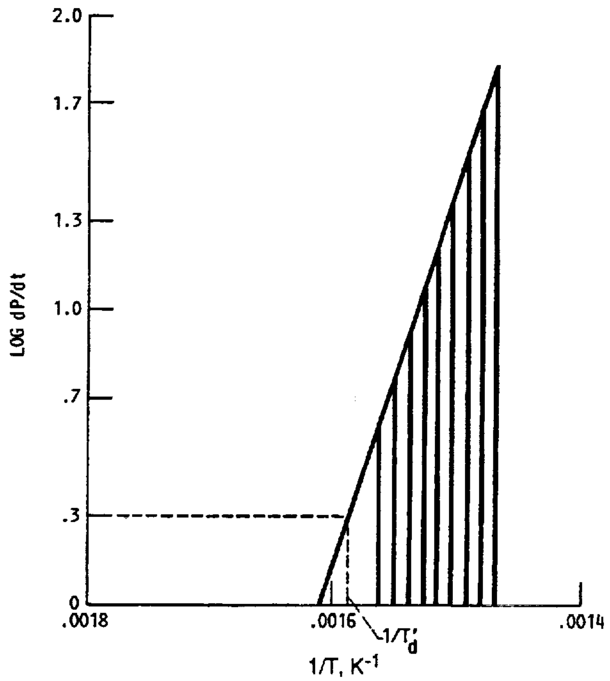


Figure 2.—Cell assembly during test.



NUMBER	TEMPERATURE, °C	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 °C

E' = 251 kJ/mol

Figure 3.—Determination of T_d' for K-6.

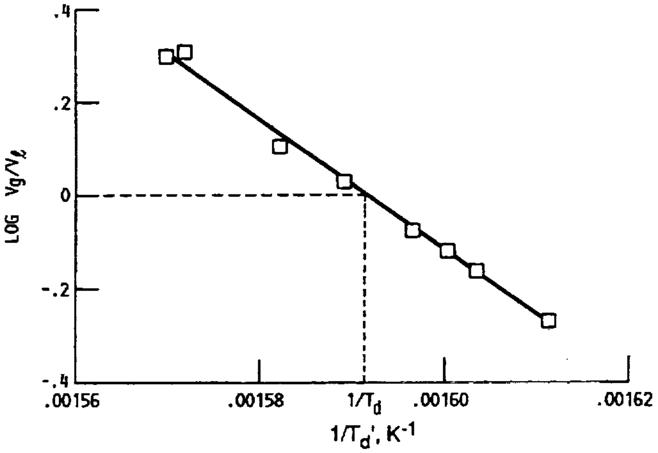


Figure 4.—Determination of T_d' for K-6. T_d = 355.2±2 °C (628.4 K); E = 269±9 kJ/mol; cor. coef. = 0.994.

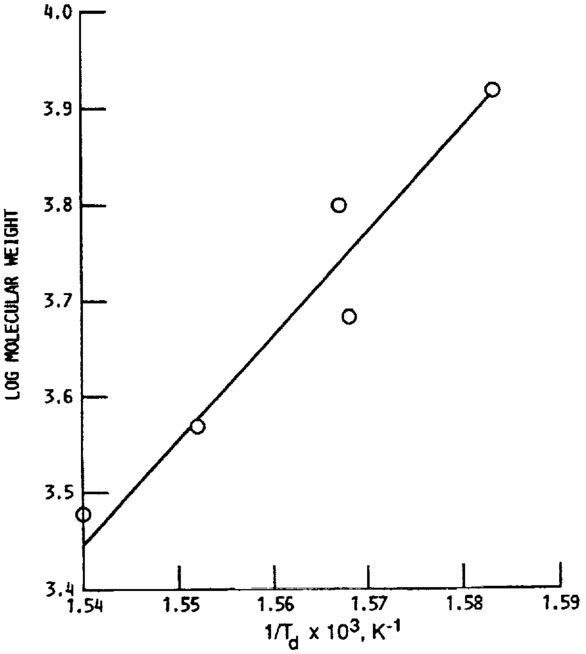


Figure 5.—Dependance of T_d on molecular weight for K fluids.

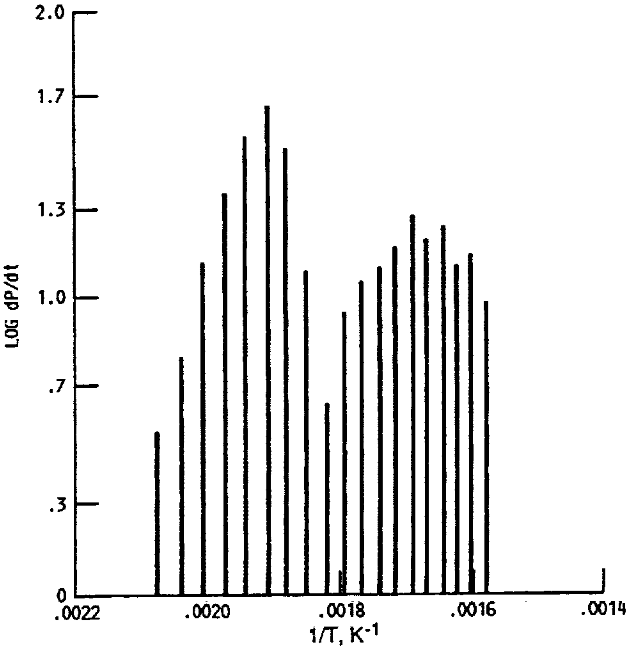


Figure 6.—Thermally unstable material in Z-2.

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13. ABSTRACT ***(Maximum 200 words)***

The thermal decomposition temperatures of several perfluoropolyalkyl ether 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 noncommercial 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 was not affected by carbon chain length, branching, or adjacent difluoroformal groups. Instead, stability was 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 two fluids supports a chain cleavage reaction mechanism for one and an unzipping reaction mechanism for the other.

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