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Determination of the Oxidative Stability of Perfluoropolyalkyl Ethers and Correlation With Chemical Structure

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DETERMINATION OF THE OXIDATIVE STABILITY OF PERFLUOROPOLYALKYL ETHERS AND CORRELATION WITH CHEMICAL STRUCTURE

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SUMMARY

The oxidative stabilities of several perfluoropolyalkyl ethers (PFPAE) with related chemical structures have been determined by thermal gravimetric analysis and correlated with their chemical structures. These results show that oxidative stability increases as the number of difluoroformal groups decreases and as trifluoromethyl substituents are added. They are also consistent with a recently proposed intramolecular disproportionation reaction mechanism involving coordination of successive ether oxygens to a Lewis acid. Since polytetrafluoroethylene contains no oxygen, it provides an indication of the upper limit to oxidative stability of PFPAE fluids. These results also show that oxidative decomposition of PFPAE fluids requires the presence of an active metal as well as air. Consequently, it may be possible to minimize decomposition and thus improve oxidative stability by passivating reactive metal surfaces.

INTRODUCTION

Perfluoropolyalkyl ethers (PFPAE) are presently being investigated for various applications in high temperature engines, space mechanisms, magnetic recording media, and hydraulic systems (refs. 1 to 11). Applications in engines are expected to involve oxidizing conditions (air and metal oxide surfaces) at temperatures up to 400 °C. Consequently, potential new lubricants must possess high oxidative stabilities in the presence of metals as well as excellent temperature/viscosity characteristics. Previous work (refs. 12 to 14) indicates that present commercially available PFPAE fluids may possess some of these critically important properties.

Thermal gravimetric analysis (TGA), (sometimes referred to as dynamic thermogravimetry) has been used for many years to study mass loss as a function of temperature for polymeric materials (ref. 15). These mass-loss versus temperature curves can be related to thermal and/or thermal-oxidative stability depending on the cover gas. Chiu (ref. 16), for example, used TGA to study the relative thermal stability of a series of solid polymers in a nitrogen atmosphere.

More recently, this technique has been used to study the relative thermal-oxidative stability of high temperature liquid lubricants (refs. 2 and 17). However, we know of no reported attempts to study the oxidative stabilities of PFPAE fluids in the presence of metals by systematically varying the chemical structure of the fluid. Therefore, the objective of this work is to establish the relationship between relative oxidative stabilities and chemical structures of PFPAE fluids in the hope that it may ultimately be possible to design and synthesize a fluid with a chemical structure that provides maximum oxidative stability under real environmental conditions.

EXPERIMENTAL

Materials

All PFPAE fluids were tested as received. Commercial fluids are represented by the symbols: DS, DD, K, Z, and Y (table I). Numbers following these symbols (e.g., DS–0, DS–1, DS–2) indicate different molecular weight fractions (table II). Names (and abbreviations) for custom synthesized fluids (table I) are as follows: perfluoropolymethylene oxide (PMO), perfluoropolyethylene oxide (PEO), perfluoropolydioxolane (DIOX), perfluoropolytrioxocane (TRIOX), perfluoropolytetraethylene glycol/formaldehyde (TEGF), and perfluoropolydipropylene glycol/formaldehyde (DPGF). Polytetrafluoroethylene (PTFE) was also analyzed because of the similarity of its chemical structure to hypothetical PFPAE fluids containing long carbon chains and thus few oxygens. Typical physical properties for all fluids are reported in tables II and III.

Thermal Gravimetric Analysis

TGA was conducted on a commercially available thermoanalyzer using 7 to 15 mg samples in 6 mm diameter platinum or aluminum sample pans under 1 atmosphere of dry nitrogen or air with a flow rate of 25 mL/min and a scan rate of 10 °C/min. Samples run in nitrogen were purged at 100 mL/min for 10 to 30 min at 200 to 300 °C to remove air. The longer purge times and higher temperatures were necessary for adequate diffusion of oxygen from the more viscous fluids. These conditions were chosen in order to determine relative oxidative stabilities of fluids with different chemical structures, not to simulate high temperature conditions in an engine, or to produce true quantitative kinetic data concerning the decomposition process.

The quartz combustion tube and platinum pan were routinely cleaned by heating to 625 °C for 10 min with a gas flow rate of 100 mL/min. The aluminum pans were cleaned before using in a commercially available ultraviolet ozone cleaning system at room temperature for 5 min, and were not reused. Longer cleaning times had no significant effect on decomposition temperatures. Empty platinum and aluminum pans showed no significant changes in weight over the temperature range of 200 to 600 °C which was routinely scanned. Variation in repeatability of TGA curves was usually ±5 °C. Generally, repeatability for the Z fluids was not as good as for D and K fluids. Proper instrument operation and calibration was confirmed by running a calcium oxalate monohydrate standard.

Nuclear Magnetic Resonance Spectra

^{19}F NMR spectra were obtained at 282.4 MHz on a 300 MHz spectrometer system. Chemical shifts (table IV) are reported relative to fluorotrichloromethane at 0 ppm.

DISCUSSION

Seventeen PFPAE fluids with related chemical structures were tested under four sets of conditions. Results obtained under each set of conditions will be discussed. Then the correlation between oxidative stability and chemical structure will be discussed. However, a little background information concerning the D fluids and TGA results must be presented first.

Structure of the D Fluids

DS–2 and DD are fluids with a similar polymeric structure, but they are made by different processes and, as indicated by ^{19}F NMR spectroscopy (table IV), differ slightly in end group structure. DS–2 afforded a spectrum essentially identical to that obtained by Kasai and Wheeler (ref. 22), showing the presence of both heptafluoro-n-propyl (−81.7, −84.0, and −130.0 ppm) and pentafluoroethyl end groups (−87.3 and −88.4 ppm) in similar amounts. Since DD has a higher molecular weight and therefore relatively fewer end groups than DS–2, one would expect weaker relative peak heights for the propyl and ethyl end groups in DD, if the structures are the same. While the signals for the propyl group were still equally intense, those for the ethyl group were much weaker, indicating that DD is terminated with a higher percentage of heptafluoro-n-propyl end groups. However, this change in end group structure would not be expected to produce a significant change in the bulk oxidative stability for DD compared with DS–2, since the D fluids are thought to decompose by a chain cleavage reaction mechanism rather than "unzipping" from the chain end (refs. 22 and 28).

Thermal Gravimetric Analysis

TGA measures the decrease in weight of a sample as temperature is increased at a constant rate. Oxidative decomposition of PFPAE fluids results in weight loss due to evaporation of the low molecular weight decomposition products. The graph of percent weight remaining versus temperature produces a TGA curve (fig. 1) which is characteristic of the fluid being tested and the experimental conditions employed. Inert conditions (e.g., platinum sample pan and nitrogen atmosphere) as well as oxidizing conditions (e.g., aluminum sample pan and air atmosphere) can be employed. It requires only milligram quantities, tests the bulk sample, and generally can be conducted in 1 to 2 hr.

The midpoint temperature ($T_{1/2}$) is the temperature at which half of the material has been lost. For decomposition reactions, $T_{1/2}$ is indicative of the relative oxidative stability of the bulk fluid in the presence of an active metal. The onset temperature (T_o) and end temperature (T_e) were determined for the step transition from the intersections of the tangents to the curve as shown in figure 1, and indicate the rate of decomposition (slope), not temperatures at which decomposition actually starts or stops. A small range (<10 °C), as generally observed for fluids containing difluoroformal groups ($-OCF_2O-$) under oxidizing conditions (table VI), indicates a rapidly accelerating reaction, and is consistent with an autocatalytic reaction.

Aluminum pans were strongly activated by decomposition of Z fluids in air, producing sharply lower decomposition temperatures if reused, but were not strongly activated by decomposition of D, K, or Y fluids. This observation is in agreement with the previously proposed (ref. 19) formation of difluoroformaldehyde during decomposition of fluids containing difluoroformal groups, followed by its reaction with aluminum oxide on the surface of the aluminum pan to produce a more reactive Lewis acid catalyst, aluminum fluoride. Furthermore, x-ray photoelectron spectroscopy (XPS), using an Al K alpha source, conducted on used aluminum pans, indicated the presence of aluminum fluoride, as previously observed by others (refs. 20 and 21). However, since aluminum pans were not reused in this study, and no attempt was made to study the aluminum pan activation phenomenon further, the data are not included in this report.

Results Under Each Set of Conditions

(1) Platinum Pan and Nitrogen.—All of the fluids were analyzed under inert conditions using a platinum pan and a dry nitrogen atmosphere. These conditions provided the reference TGA curves

(table V) necessary for interpretation of the curves obtained under other conditions. Decomposition was indicated if a TGA curve obtained under other conditions appeared at a sharply lower temperature than the corresponding one obtained under these inert conditions.

(2) Aluminum Pan and Air.—All of the fluids were analyzed in the presence of an active metal under oxidizing conditions using an aluminum pan and a dry air atmosphere. Comparison of the midpoint temperatures of the TGA curves thus obtained (table VI) with the corresponding midpoint temperatures of the curves obtained under inert conditions shows that all of the curves except those for DS–0, DS–1, the K fluids, TEGF, DPGF, and PTFE occur at sharply lower temperatures (table IX). This indicates that these fluids (table IX) are undergoing oxidative decomposition, as previously reported for the Y and Z fluids (ref. 23), and provides an indication of their relative oxidative stabilities. Furthermore, since the data have been obtained under similar conditions for a variety of fluids with comparable structures, it should be possible to begin to draw conclusions concerning the effect of structure on oxidative stability.

Several other trends in the data (table VI) can also be observed. For the Z fluids, the decomposition temperature is nearly independent of molecular weight, as might be expected for fluids containing difluoroformal groups which undergo a rapidly accelerating self-catalyzed decomposition reaction to produce volatile products. DS–0 and DS–1 are lower molecular weight fluids than DS–2. Absence of a large change in their midpoint temperatures indicates that they simply evaporate before reaching a high enough temperature (422 °C shown by DS–2) to decompose. TEGF and DPGF are the lowest boiling of all of the custom synthesized fluids (table III). The small reduction in their midpoint temperatures indicate that they may also be evaporating, but the sharply reduced end temperatures suggest that some decomposition is also occurring. These results also confirm that the K fluids are very stable to oxidative decomposition, as previously reported (ref. 1). PTFE is more stable to oxidizing conditions than any of the fluids tested. Therefore, it provides an indication of the upper limit to oxidative stability that can be achieved with PFPAE fluids.

(3) Platinum Pan and Air.—In order to determine if oxidative decomposition is simply a result of air oxidation alone and does not actually involve the aluminum metal or aluminum oxide surface of the pan, nine PFPAE fluids were tested in the presence of an inert metal under oxidizing conditions (platinum pan and dry air atmosphere). The similarity of TGA curves obtained (table VII) with the corresponding ones in platinum pans in nitrogen confirms that all of these fluids are stable to air oxidation in the presence of inert metal surfaces at these temperatures, as previously reported for the Y and Z fluids (ref. 23). Consequently, decomposition under oxidizing conditions must not be due solely to the presence of air, but must involve the aluminum metal or aluminum oxide surface of the metal pan.

(4) Aluminum Pan and Nitrogen.—In order to determine if oxidative decomposition is simply a Lewis acid catalyzed decomposition of the fluid by the metal oxide surface of the pan that does not actually involve oxygen in the air, nine PFPAE fluids were also tested with an active metal under an inert atmosphere (aluminum pan in nitrogen). Comparing the TGA curves thus obtained (table VIII) to those in platinum pans in nitrogen shows no large reductions in temperature and therefore little if any Lewis acid catalysis. However, others using α–aluminum oxide powder have observed Lewis acid catalysis of the Z fluids (ref. 21). Our failure to detect significant catalysis of the Z fluids could be due to the difference in crystal structure between α–aluminum oxide and the aluminum oxide on aluminum metal surfaces (ref. 19), or to the relatively small surface area of the pans compared to powder.

The failure of PFPAE fluids to react as rapidly with aluminum pans in nitrogen as with aluminum pans in air indicates that it is not simply a Lewis acid catalyzed decomposition by the aluminum oxide surface alone which is being observed under oxidizing conditions, but an oxidative decomposition involving both oxygen and aluminum of the pan. Consequently, it may be possible to significantly improve the oxidative stability of PFPAE fluids in the presence of reactive metals by passivating the reactive metal surfaces, as has been suggested by others (refs. 20, 24, and 25).

Correlation of Oxidative Stability and Chemical Structure

The relative oxidative stabilities, as indicated by the midpoint temperatures, of all of the materials studied increase in the following order: PMO < Z < DIOX ≈ TRIOX ≈ TEGF ≈ DPGF ≈ Y < DS < PEO < DD < K < PTFE (table VI, fig. 2). From this order of relative stabilities, two trends involving chemical structure can be clearly identified:

(1) Oxidative stability increases as the percentage of difluoroformal groups decreases. All of the units in PMO are difluoroformal groups. Sixty percent are difluoroformal groups in the Z fluids. Fifty percent or less are difluoroformal groups in DIOX, TRIOX, TEGF, DPGF, and Y. No units are difluoroformal groups in DS, PEO, DD, K, and PTFE.

(2) Oxidative stability increases with the addition of a trifluoromethyl substituent next to the oxygen. PEO and K both have a two carbon monomer backbone with no difuoroformal groups, but the more stable K has a trifluoromethyl substituent. The same is true for DPGF and Y compared with Z. However, the increase in stability could also be attributed to the decrease in the percentage of difluoroformal groups in this case.

This order of stability is also consistent with the intramolecular Lewis acid-catalyzed disproportionation reaction mechanism proposed by Kasai, Wing, and Wheeler (fig. 3, ref. 21). The lowest energy conformations of the ether backbone occur when the molecule lies in a zig zag pattern (refs. 26 and 27). Furthermore, the molecule should be most reactive when successive oxygens lie on the same side of the molecule and can coordinate with the Lewis acid catalyst. This situation exists when there are an odd number of carbons (one or three) in the monomer unit. Compounds containing an even number of carbons (two) will have successive oxygens on opposite sides of the molecule. Since these successive oxygens can not readily complex with the Lewis acid catalyst, these compounds should be less reactive. Thus, one would expect that reactivity should decrease as the percentage of one carbon monomer units decreases (PMO > Z > DIOX, TRIOX, TEGF) and that these compounds in turn should be more reactive than those containing two carbon monomer units (PEO), as is indeed observed. Similarly, polymers with monomer units containing three carbons (DS–2 and DD) might also be expected to be more reactive than those containing two carbons (PEO). However, since the three carbon fluids (DS–2 and DD) exhibit reactivities which are greater (DS–2) as well less (DD) than the two carbon fluid PEO, it is not clear from this data whether this factor is indeed the dominating one or whether other factors may also be involved. Part of the relatively high stability of the DD fluid, for example, may be due to its significantly higher molecular weight which would require more cleavages, and thus more time, to produce volatile products. The change in end group structure from ethyl and propyl groups in DS–2 to primarily propyl groups in DD would not be expected to produce a significant difference in bulk oxidative stability since the D fluids are thought to decompose by a chain cleavage reaction mechanism rather than "unzipping" from the end of the chain (refs. 22 and 28).

The presence of a trifluoromethyl substituent on a two carbon backbone (K fluids) increases thermal stability significantly relative to a fluid with no substituent on a two carbon backbone (PEO), although both decompose by an unzipping mechanism. Both ends of the PEO molecule are identical. Consequently, PEO can unzip from either end. However, the trifluoromethyl substituent next to the oxygen of the K fluid results in the two ends being different, and prevents the molecule from unzipping from one end, which reduces its reactivity (refs. 27 and 29).

Finally, PTFE, containing no ether oxygens and therefore no reactive sites, is the least reactive of all of the compounds studied, and gives an indication of the upper limit of oxidative stability of hypothetical polyethers with long carbon chains in the monomer units.

Some structural characteristics apparently necessary to produce maximum oxidative stability, such as eliminating difluoroformal groups and adding trifluoromethyl substituents, are just the opposite of those required for maximizing temperature/viscosity and volatility characteristics (ref. 4). Consequently, it is clear that compromises will need to be made in designing a fluid with the most beneficial overall properties for a specific application. On the other hand, it should be kept in mind that these fluids do not undergo oxidative decomposition in air in the absence of a reactive metal. Therefore, it may be possible to use these fluids in applications where maximum temperature/viscosity and volatility characteristics are required if reactive metal surfaces can be passivated via surface modification techniques or soluble inhibitors.

CONCLUSIONS

1. Correlation of oxidative stabilities and chemical structures shows that oxidative stability can be increased by eliminating difluoroformal groups and adding trifluoromethyl substituents.

2. Since oxidative decomposition involves ether type oxygens, and since PTFE contains no ether oxygens at all, it provides an indication of the upper limit to oxidative stability that can be achieved by increasing the carbon chain length in PFPAE fluids.

3. Oxidative decomposition of PFPAE fluids requires the presence of a reactive metal as well as air. Consequently, oxidative stability might be improved if reactive metal surfaces can be passivated.

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TABLE I.—PRIMARY CHEMICAL STRUCTURES OF PFPAE FLUIDS

Fluid	Structure
DS	$C_3F_7O(CF_2CF_2CF_2O)_XC_2F_5$
DD	$C_3F_7O(CF_2CF_2CF_2O)_XC_3F_7$
K	$C_3F_7O[CF(CF_3)CF_2O]_XC_2F_5$
Z	$CF_3O(CF_2CF_2O)_X(CF_2O)_YCF_3$ X/Y=2/3
Y	$C_3F_7O[CF(CF_3)CF_2O]_M(CF_2O)_NCF_3$ M/N=40/1
PMO	$CF_3O(CF_2O)_XCF_3$
PEO	$CF_3O(CF_2CF_2O)_XCF_3$
DIOX	$CF_3O(CF_2CF_2OCF_2O)_XCF_3$
TRIOX	$CF_3O[(CF_2CF_2O)_2CF_2O]_XCF_3$
TEGF	$CF_3O[(CF_2CF_2O)_4CF_2O]_XCF_3$
DPGF	$CF_3O\{[CF(CF_3)CF_2O]_2CF_2O\}_XCF_3$
PTFE	$CF_3(CF_2)_XCF_3$

TABLE II.—PHYSICAL PROPERTIES OF COMMERCIAL PFPAE FLUIDS

Fluid	Average Molecular Weight (g/mol)	Kinematic Viscosity mm^2/s (cSt) at 20 °C
DS-0	4 500	150
DS-1	5 600	250
DS-2	8 400	500
DD	14 000	600
K-1	8 250	1 600
K-2	11 000	2 717
K-3	--------	-------
Z-1	8 000	148
Z-2	9 500	250
Z-3	13 000	560
Y	6 000 to 7 000	1 000 to 2 000

TABLE III.—PHYSICAL PROPERTIES OF CUSTOM SYNTHESIZED PFPAE FLUIDS

Fluid	Boiling Point Range °C at 6.67 Pa (0.05 torr)	Avg. MW (g/mol)	Kinematic Viscosity mm^2/s (cSt) at 20 °C
PMO	>310	6 000	-----
PEO	>343	8 000	447
DIOX	>343	8 000 to 9 000	238
TRIOX	>370	9 000 to 10 000	502
TEGF	>300	6 000	33
DPGF	>300	5 000	-----

TABLE IV.—^{19}F NMR SPECTRA

Fluid and Structure	Group	Chemical Shift (ppm)	Relative Peak Heights (%)
DS-2 $CF_3CF_2CF_2O(CF_2CF_2CF_2O)_XCF_2CF_3$ 1 2 3 4 5 6 7 8	1	−81.7	1.7
	2	−130.0	1.5
	3	−84.0	0.8
	4,6	−83.0	100.0
	5	−129.0	60.0
	7	−88.4	0.8
	8	−87.3	2.5
DD $CF_3CF_2CF_2O(CF_2CF_2CF_2O)_XCF_2CF_2CF_3$ 1 2 3 4 5 6 3 2 1 $-OCF_2CF_3$ 7 8	1	−81.7	1.7
	2	−130.0	1.2
	3	−84.0	0.8
	4,6	−83.0	100.0
	5	−129.0	51.0
	7	−88.3	0.3
	8	−87.3	0.3

TABLE V.—ONSET (T_o), MIDPOINT ($T_{1/2}$), AND END (T_e) TEMPERATURES (°C) FOR PFPAE FLUIDS IN PLATINUM PANS AND NITROGEN ATMOSPHERE

Fluid	T_o	$T_{1/2}$	T_e
DS-0	313	378	444
DS-1	380	412	444
DS-2	436	469	502
DD	507	542	577
K-1	410	442	474
K-2	461	490	519
K-3	478	508	539
Z-1	401	455	516
Z-2	443	474	510
Z-3	464	493	524
Y	406	446	487
PMO	374	395	416
PEO	420	467	513
DIOX	415	474	534
TRIOX	457	496	535
TEGF	360	415	469
DPGF	370	409	449
PTFE	552	580	608

TABLE VI.—ONSET (T_o), MIDPOINT ($T_{1/2}$), AND END (T_e) TEMPERATURES (°C) FOR PFPAE FLUIDS IN ALUMINUM PANS AND AIR ATMOSPHERE

Fluid	T_o	$T_{1/2}$	T_e
DS-0	300	369	438
DS-1	394	406	429
DS-2	417	422	427
DD	463	474	490
K-1	401	427	454
K-2	452	479	506
K-3	473	500	528
Z-1	376	381	386
Z-2	381	385	389
Z-3	384	387	389
Y	386	393	399
PMO	346	348	349
PEO	412	436	459
DIOX	392	395	397
TRIOX	387	391	394
TEGF	397	400	405
DPGF	383	391	399
PTFE	560	570	589

TABLE VII.—ONSET (T_o), MIDPOINT ($T_{1/2}$), AND END (T_e) TEMPERATURES (°C) FOR PFPAE FLUIDS IN PLATINUM PANS AND AIR ATMOSPHERE

Fluid	T_o	$T_{1/2}$	T_e
DS-1	374	407	440
DS-2	430	463	496
DD	502	536	573
K-1	406	440	474
K-2	459	490	521
K-3	476	507	538
Z-1	416	460	518
Z-2	452	479	512
Z-3	457	490	524

TABLE VII.—ONSET (T_o), MIDPOINT ($T_{1/2}$), AND END (T_e) TEMPERATURES (°C) FOR PFPAE FLUIDS IN ALUMINUM PANS AND NITROGEN ATMOSPHERE

Fluid	T_o	$T_{1/2}$	T_e
DS-1	369	401	433
DS-2	422	456	491
DD	485	520	555
K-1	400	434	467
K-2	448	477	506
K-3	473	499	527
Z-1	413	444	490
Z-2	434	478	525
Z-3	461	495	535

TABLE IX.—LARGE DECREASE IN MIDPOINT TEMPERATURES (°C) UNDER OXIDIZING CONDITIONS COMPARED TO INERT CONDITIONS INDICATES OXIDATIVE DECOMPOSITION

Fluid	$T_{1/2}$ Under Inert Conditions	$T_{1/2}$ Under Oxidizing Conditions	Difference
DS-2	469	422	47
DD	542	474	68
Z-1	455	381	74
Z-2	474	385	89
Z-3	493	387	106
Y	446	393	53
PMO	395	348	47
PEO	467	436	31
DIOX	474	395	79
TRIOX	496	391	105

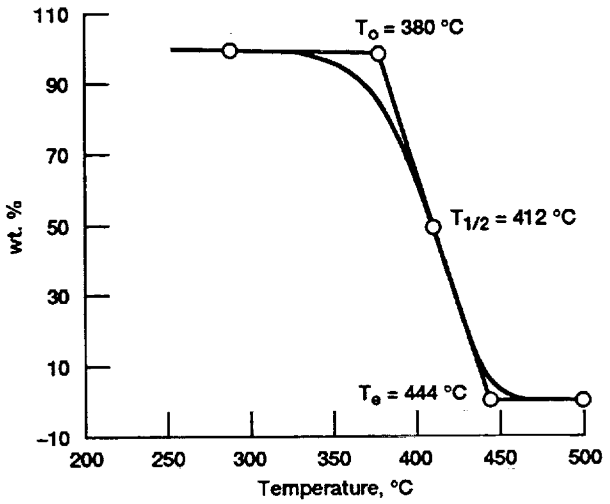

Figure 1.—TG analysis of liquid lubricant (DS-1 in Pt pan and nitrogen) illustrating onset temperature (T_o), midpoint temperature ($T_{1/2}$), and end temperature (T_e).

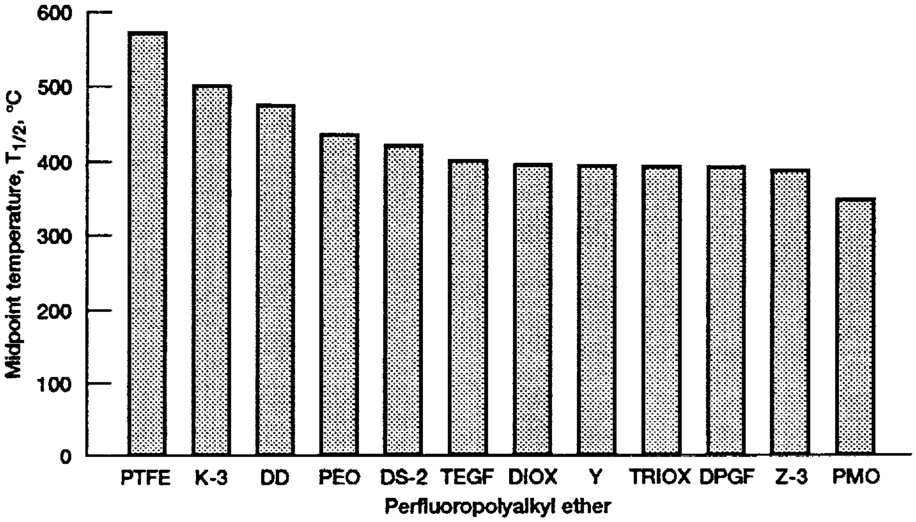

Figure 2.—Midpoint temperatures of perfluoropolyalkyl ethers, °C.

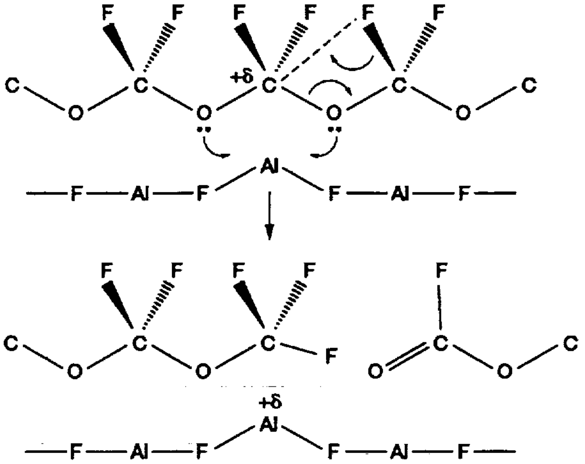

Figure 3.—Intramolecular Lewis acid-catalyzed disproportionation reaction mechanism (ref. 21).

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

The oxidative stabilities of several perfluoropolyalkyl ethers (PFPAE) with related chemical structures have been determined by thermal gravimetric analysis and correlated with their chemical structures. These results show that oxidative stability increases as the number of difluoroformal groups decreases and as trifluoromethyl substituents are added. They are also consistent with a recently proposed intramolecular disproportionation reaction mechanism involving coordination of successive ether oxygens to a Lewis acid. Since polytetrafluoroethylene contains no oxygen, it provides an indication of the upper limit to oxidative stability of PFPAE fluids. These results also show that oxidative decomposition of PFPAE fluids requires the presence of an active metal as well as air. Consequently, it may be possible to minimize decomposition and thus improve oxidative stability by passivating reactive metal surfaces.

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