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Heterolytic C–F bond energies and stabilities of poly(perfluoroethers)

Bruce E. Smart and David A. Dixon
*Du Pont Central Research & Development, Experimental Station, Wilmington, DE 19880-0328 (USA)**

Abstract

The heterolytic strengths of various C–F bonds adjacent to oxygen in the perfluoroethers CF_3OCF_3, $CF_3OCF_2CF_3$, $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2OCF_3$ and $CF_3OCF_2CF(CF_3)OCF_3$ have been calculated at the MP-2 level with a polarized double-ζ basis set. These C–F bonds all have similar strengths (233–238 kcal/mol), except for the much weaker methylene C–F bonds (222.6 kcal/mol) in $CF_3OCF_2OCF_3$, and the stronger methine C–F bond (244.5 kcal/mol) in $CF_3OCF_2CF(CF_3)OCF_3$. These bond strengths are related to the experimental stabilities of commercial Fomblin®, Krytox® and Demnum® poly(perfluoroethers). An electrophilic decomposition mechanism involving assisted heterolysis of C–F bonds is proposed.

Introduction

Poly(perfluoroethers) are commercially important materials with generally excellent thermal and chemical stabilities that have diverse applications, including surface lubricants in magnetic recording media [1], diffusion pump oils [2, 3], dielectric fluids [4], and high-temperature hydraulic fluids and greases [5, 6]. The most common types of poly(perfluoroether) are the Fomblin® Z and Y, Krytox® and Demnum® materials. The inherent thermal stabilities of these structures are similar (dec. > 350 °C [6, 7]), but their stabilities in the presence of metals or Lewis acids differ markedly. For example, Fomblin® Z completely degrades in the presence of ferrous alloys at 315 °C [5] and Fe_2O_3 at 185 °C [8], whereas Krytox® and Demnum® undergo <5% degradation under the same conditions [6, 8]. The decomposition of Fomblin® Z can be catalyzed by $AlCl_3$ at temperatures as low as 100 °C [9]. The acetal units $-OCF_2O-$ in the polymer backbone obviously are reactive sites, although the decomposition mechanism has not been elucidated. It has been postulated that the poly(perfluoroether) structures all have polar C–O bonds that are susceptible to attack by Lewis acids through coordination to the oxygen lone pairs, but in the case of the Krytox® polymer, the CF_3 groups help to sterically shield the oxygens from attack [10, 11].

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$CF_3O(CF_2CF_2O)_x(CF_2O)_yCF_3$

Fomblin^R Z($x/y \cong 2/3$)

$C_3F_7O[CF(CF_3)CF_2O]_xC_2F_5$

Krytox^R

$CF_3O[CF(CF_3)CF_2O]_x(CF_2O)_yCF_3$

Fomblin^R Y($x/y \cong 40/1$)

$C_3F_7O(CF_2CF_2CF_2O)_xC_2F_5$

Demnum^R

Another plausible mechanism might involve attack by metal or Lewis acid on a fluorine atom adjacent to oxygen to generate a short-lived carbocation intermediate that cleaves to produce an acid fluoride group (eqn. 1).

$$\begin{aligned}&-CF_2OCF_2- \xrightarrow{MX_n} [-\overset{+}{C}FOCF_2-]MX_nF^- \\ &\longrightarrow -\overset{\overset{\displaystyle O}{\|}}{C}F + [\overset{+}{C}F_2-]MX_nF^- \xrightarrow{-MX_n} CF_3^-\end{aligned} \qquad (1)$$

The report that alkyl fluoroalkyl ethers XCF_2OR ($R = CH_3$ or C_2H_5) rapidly lose CH_3F or C_2H_5F in the presence of catalytic Lewis acids like SbF_5 at room temperature or below via a cationic process [12] is a good precedent for this alternative mechanism. The relatively high lability of the acetal group therefore could be simply attributed to its lower heterolytic C–F bond strength, arising primarily from the greater stability of $-O\overset{+}{C}FO-$ *vs.* $-OCF_2\overset{+}{C}FO-$ or $-OCF_2\overset{+}{C}(CF_3)O-$ cations, of course, assuming that adjacent perfluoroalkoxy groups stabilize carbocation centers. This assumption, however, may not be valid since it is known that, at least in an electrophilic aromatic substitution, the CF_3O group is net electron withdrawing ($\sigma_p^+ = 0.067$) in contrast to F($\sigma_p^+ = -0.073$) [13].

To probe the effect of the ether structure on reactivity and carbocation stability, we have calculated the C–F heterolytic bond strengths in CF_3CF_3, CF_3OCF_3 and $CF_3OCF_2CF_3$, and in the $CF_3OCF_2OCF_3$, $CF_3OCF_2CF_2OCF_3$ and $CF_3OCF_2CF(CF_3)OCF_3$ model compounds for the Fomblin^R and Krytox^R poly(perfluoroethers).

Calculations

Calculations were preformed with GRADSCF [14]* on Cray X-MP and Y-MP computers in a single processor mode. The geometries of the molecules were gradient optimized [15] and force fields [16] were obtained analytically with a double-ζ basis set augmented by a set of d polarization functions on each carbon ($DZ + D_c$) [17]. This basis set has proved to give good geometry predictions for a wide range of fluorocarbons [18]. Correlation corrections to the final energies were made at the MP-2 level [19] for

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*Designed and written by A Komornicki

TABLE 1

Electronic energies

Compound	$DZ + D_c$ total energy (a u)		Zero-point energy (kcal/mol)
	SCF	MP-2	
CF_4	−435.710142	−436.258359	10.7
CF_3CF_3	−672.486903	−673.370818	18.5
CF_3OCF_3	−747.382022	−748.434321	21.4
$CF_3OCF_2CF_3$	−984.160705	−985.548856	29.1
$CF_3OCF_2OCF_3$	−1059.053492	−1060.609860	32.1
$CF_3OCF_2CF_2OCF_3$	−1295.834166	−1297.726582	39.8
$CF_3OCF_2CF(CF_3)OCF_3$	−1532.608795	−1534.840950	47.4
CF_3^+	−335.834263	−336.273196	8.9
$CF_3CF_2^+$	−572.609505	−573.380256	16.2
$CF_3OCF_2^+$	−647.543615	−648.484427	19.4
$CF_3O\overset{+}{C}FCF_3$	−884.319532	−885.595517	26.8
$CF_3O\overset{+}{C}FCF_2OCF_3$	−959.240207	−960.682993	30.0
$CF_3O\overset{+}{C}FCF(CF_3)OCF_3$	−1432.775261	−1434.895483	45.1
$CF_3OCF2\overset{+}{C}(CF_3)OCF_3$	−1432.760866	−1434.877893	44.9

all of the valence electrons, and all computed reaction energies were corrected for zero-point energy differences. The electronic energies of the fluorinated molecules for this study are given in Table 1.

Rather than directly calculating absolute heterolytic bond dissociation energies (ΔH° for reaction 2), which would require very accurate calculations of F^-, bond dissociation energies (BDE) relative to CF_4 heterolysis were computed. The ΔH° for isodesmic reaction 3 gives the heterolytic BDE of A–F relative to that for CF_4, which is experimentally 258.9 kcal/mol from the heats of formation of CF_3^+, F^- and CF_4 [20].

$$A\text{–}F \longrightarrow A^+ + F^- \tag{2}$$

$$CF_3^+ + A\text{–}F \longrightarrow CF_4 + A^+ \tag{3}$$

Results and discussion

Geometries

The geometries of the various perfluoroethers have been calculated with a variety of basis sets [10, 11, 21], and the previously reported 3-21G geometries [10] agree reasonably well with those calculated here with the larger $DZ + D_c$ basis set. Some featured geometry parameters for the optimized structures are listed in Tables 2 to 6. The C–F and C–O distances generally are shorter with the larger basis set, whereas the C–C distances tend to be shorter with the 3-21G basis set. This is rather surprising and implies steric interactions are handled somewhat differently with the smaller basis set. The conformations of the molecules computed with the two basis sets are similar, except for $CF_3OCF_2OCF_3$. For this ether, four conformations were investigated and no evidence was found for the expected anomeric effect that prevails in $CH_3OCH_2OCH_3$ [22].*

The geometries of the carbocations have several interesting features (Tables 2 to 6). The $^+C–F$ bond lengths are always very short, 1.248 Å in $CF_3OCF_2^+$ and 1.220 Å in CF_3^+ (1.218 Å at the 6-31G* level [23]), for instance. These values are much shorter than C–F bond lengths in neutral

TABLE 2

Geometrical parameters[a] for CF_3OCF_3 and $CF_3OCF_2^+$

Parameter	C_1OC_2	$C_1OC_2^+$
$r(C_2–F)$	1 311[b] (1 330)[b,c]	1 248
$r(C_1–O)$	1 357 (1 370)	1 501
$r(C_2–O)$	1 357 (1 370)	1 227
$\angle(C_1OC_2)$	122 1 (124 1)	126 3
$\tau(C_1–O)$[d]	−161.0	179 0
$\tau(C_2–O)$[d]	−161 0	−179 5

[a] Bond distances in angstrom, bond angles in degrees, here and in Tables 3–6
[b] Average C–F value
[c] 3-21G values [10] in parentheses
[d] Largest C–O torsional angle

TABLE 3

Geometrical parameters for $CF_3OCF_2CF_3$ and $CF_3O\overset{+}{C}FCF_3$

Parameter	$C_1OC_2C_3$	$C_1O\overset{+}{C}_2C_3$
$r(C_2–F)$	1 323[a] (1 347)[a]	1 248
$r(C_1–O)$	1 359 (1 373)	1 506
$r(C_2–O)$	1 358 (1 375)	1 224
$r(C_2–C_3)$	1 546 (1 505)	1 575
$\angle(OC_2C_3)$	107 4 (106 8)	120 9
$\angle(C_1OC_2)$	122 4 (124 0)	126 8
$\tau(C_1–O)$	161 2	179 7
$\tau(C_2–O)$	160 9	−180 0
$\tau(C_2–C_3)$	179 0	−0 5

[a] Average C–F value

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*Details of these calculations and the electronic properties of $CF_3OCF_2OCF_3$ *vs* $CH_3OCH_2OCH_3$ that relate to the anomeric effect will be published elsewhere

TABLE 4

Geometrical parameters for $CF_3OCF_2OCF_3$ and $CF_3O\overset{+}{C}FOCF_3$

Parameter	$C_1O_1C_2O_2C_3$	$C_1O_1\overset{+}{C}_2O_2C_3$
$r(C_2\text{–}F)$	1.317[a] (1.336)[a]	1.257
$r(C_1\text{–}O_1)$	1.357 (1.371)	1.459
$r(C_2\text{–}O_1)$	1.356 (1.374)	1.248
$r(C_2\text{–}O_2)$	1.362 (1.374)	1.248
$r(C_3\text{–}O_2)$	1.358 (1.371)	1.459
$\angle(C_1O_1C_2)$	122.8 (124.5)	125.2
$\angle(O_1C_2O_2)$	109.1 (111.5)	118.5
$\angle(C_2O_2C_3)$	122.1	125.1
$\tau(C_1\text{–}O_1)$	−168.9	−180.0
$\tau(C_2\text{–}O_1)$	78.5	−180.0
$\tau(C_2\text{–}O_2)$	−163.9	180.0
$\tau(C_3\text{–}O_2)$	−162.0	180.0

[a] Average C–F value.

TABLE 5

Geometrical parameters for $CF_3OCF_2CF_2OCF_3$ and $CF_3OCF_2\overset{+}{C}FOCF_3$

Parameter	$C_1O_1C_2C_3O_2C_4$	$C_1O_1C_2\overset{+}{C}_3O_2C_4$
$r(C_3\text{–}F)$	1.322[a] (1.345)[a]	1.247
$r(C_1\text{–}O_1)$	1.359 (1.373)	1.403
$r(C_2\text{–}O_1)$	1.358 (1.377)	1.335
$r(C_3\text{–}O_2)$	1.358 (1.377)	1.226
$r(C_4\text{–}O_2)$	1.359 (1.373)	1.496
$r(C_2\text{–}C_3)$	1.547 (1.506)	1.568
$\angle(C_1O_1C_2)$	122.4 (124.0)	122.4
$\angle(O_1C_2O_3)$	107.1 (106.4)	103.6
$\angle(C_2C_3O_2)$	107.1 (106.4)	120.8
$\angle(C_3O_2C_4)$	122.4 (124.0)	126.6
$\tau(C_1\text{–}O_1)$	161.5	−159.2
$\tau(C_2\text{–}O_1)$	160.5	165.2
$\tau(C_3\text{–}O_2)$	−160.5	−179.3
$\tau(C_4\text{–}O_2)$	−161.6	−179.1
$\tau(C_2\text{–}C_3)$	180.0	116.4

[a] Average $C_{2,3}$–F value.

perfluorinated systems, which usually range from 1.30 to 1.36 Å [24], and reflect the contribution of p–π electron donation from a fluorine lone pair to the vacant orbital on carbon. The C–O bond lengths differ considerably, depending upon whether oxygen is bonded to uncharged or charged carbon. For $CF_3OCF_2{}^+$, the $^+$C–O bond distance is 0.13 Å *shorter* than the C–O distance in CF_3OCF_3, whereas the other C–O bond is 0.14 Å *longer* than in CF_3OCF_3 (Table 2). The COC bond angle in $CF_3OCF_2{}^+$ opens up

TABLE 6

Geometrical parameters for $CF_3OCF(CF_3)CF_2OCF_3$, $CF_3OC(CF_3)CF_2OCF_3$ and $CF_3OCF(CF_3)\overset{+}{C}FOCF_3$

Parameter	$C_1O_1\overset{\overset{C_3}{\vert}}{C_2}C_4O_2C_5$	$C_1O_1\overset{\overset{C_3}{\vert}}{\overset{+}{C}_2}C_4O_2C_5$	$C_1O_1\overset{\overset{C_3}{\vert}}{C_2}C_4O_2C_5$
$r(C_2–F)$	1.335 (1.359)	–	1.320
$r(C_4–F)$	1.323[a] (1.344)[a]	1.311[a]	1.249
$r(C_1–O_1)$	1.357 (1.371)	1.509	1.394
$r(C_2–O_1)$	1.378 (1.392)	1.224	1.353
$r(C_4–O_2)$	1.357 (1.379)	1.339	1.226
$r(C_5–O_2)$	1.361 (1.375)	1.401	1.494
$r(C_2–C_3)$	1.556 (1.518)	1.579	1.578
$r(C_2–C_4)$	1.557 (1.515)	1.568	1.563
$\angle(C_1O_1C_2)$	124.0	133.4	122.9
$\angle(O_1C_2C_3)$	106.8	125.0	116.4
$\angle(O_1C_2C_4)$	107.2	115.1	102.0
$\angle(C_2C_4O_2)$	108.4	103.3	120.5
$\angle(C_4O_2C_5)$	122.4	122.5	126.5
$\tau(C_1–O_1)$	178.5	−162.4	−162.5
$\tau(C_2–O_1)$	−116.7	179.6	−165.3
$\tau(C_4–O_2)$	−159.5	−163.3	−179.1
$\tau(C_5–O_2)$	−162.1	−158.1	−177.0
$\tau(C_2–C_3)$	175.8	−155.8	148.7
$\tau(C_2–C_4)$	176.6	103.7	123.5

[a] Average C–F value

by only 4° as compared to CF_3OCF_3. Similar trends are observed for the other fluoroether cations. For $CF_3O\overset{+}{C}FOCF_3$, the $^+C–O$ bond shortening and $C–O(CF_3)$ lengthening are less pronounced than in $CF_3OCF_2^+$, which is consistent with charge being delocalized onto *both* CF_3O groups.

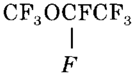
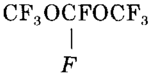
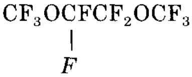
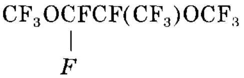
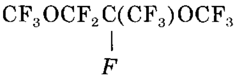
These structural features clearly show the importance of p–π donation from oxygen lone pairs in a CF_3O group to the vacant p-orbital on C^+. The energetic consequences of this delocalization are addressed in the following section.

Heterolytic bond energies

The heterolytic C–F BDEs for fluorine adjacent to the ether oxygen (Table 7) are all substantially lower than the C–F BDEs in CF_4 or CF_3CF_3 (260.9 kcal/mol). The 22 kcal/mol difference between $CF_3OCF_2–F$ and $CF_3–F$ BDEs (Table 7; eqn. 4) clearly indicates that, unlike electrophilic aromatic substitution (see above), p–π donation from the CF_3O group dominates its electron-withdrawing inductive effect and CF_3O is considerably more stabilizing than F when directly bonded to a saturated carbocation center. Moreover, two CF_3O groups bonded to an electron-deficient

TABLE 7

Calculated heterolytic C–F bond dissociation energies

Structure	BDE (kcal/mol)[a]
CF_3OCF_2–*F*	236.6
 $CF_3O\underset{\displaystyle F}{\underset{\mid}{C}}FCF_3$	238.4
 $CF_3O\underset{\displaystyle F}{\underset{\mid}{C}}FOCF_3$	222.6
 $CF_3O\underset{\displaystyle F}{\underset{\mid}{C}}FCF_2OCF_3$	235.6
 $CF_3O\underset{\displaystyle F}{\underset{\mid}{C}}FCF(CF_3)OCF_3$	233.3
 $CF_3OCF_2\underset{\displaystyle F}{\underset{\mid}{C}}(CF_3)OCF_3$	244.5

[a]Relative to CF_3–*F* (258.9 kcal/mol); see text.

carbon are significantly more stabilizing than one (eqn. 5).

$$CF_3^+ + CF_3OCF_3 \longrightarrow CF_4 + CF_3OCF_2^+ \quad (\Delta H^\circ = -22.3\ \text{kcal/mol}) \qquad (4)$$

$$CF_3OCF_2^+ + CF_3OCF_2OCF_3 \longrightarrow CF_3OCF_3 + CF_3O\overset{+}{C}FOCF_3 \quad (\Delta H^\circ = -14.0\ \text{kcal/mol}) \qquad (5)$$

The calculated heterolytic C–F BDEs for the CF_2 and CF_3 groups adjacent to oxygen are very similar (233 to 238 kcal/mol) in all the model perfluoroethers, with the notable exception of $CF_3OCF_2OCF_3$, whose methylene C–F bonds are comparatively much weaker (*ca.* 223 kcal/mol). This is fully consistent with experimental data on the lability of the $-OCF_2O-$ acetal groups and the proposed electrophilic mechanism for degradation of the poly(perfluoroethers) (eqn. 1).

Finally, for the Krytox^R model structure $CF_3OCF_2CF(CF_3)OCF_3$, it is notable that although the *tert*-CF bond is the longest C–F bond in any of the model structures, its heterolytic bond strength is by far the highest (244.5 kcal/mol). With the reasonable assumption that kinetic reactivity correlates with bond strength, this implies it is very unlikely that metals or Lewis acids will competitively attack the tert-CF bonds in Krytox^R. Even though the model calculations show the methylene CF bonds in Krytox^R are inherently no stronger than those in the $-OCF_2CF_2O-$ or

$-OCF_2CF_2CF_2O-$ groups, it is likely that the adjacent CF_3 groups to some degree sterically shield the CF_2 groups toward attack, and Krytox® therefore is expected to be at least as, if not more, stable than the other poly(perfluoroethers) in the presence of metals or Lewis acids.

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