The Thermal Decomposition of Perfluoroesters

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Certain hydrocarbon esters are known to decompose into carboxylic acids and olefins at elevated temperatures. Mechanistic studies revealed that the decomposition proceeds intramolecularly via the transition state **TS-1** with the migration of one of the β-hydrogen atoms.[1]
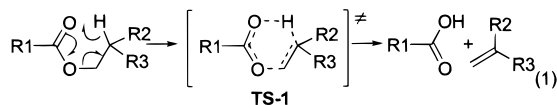
This knowledge led to the development of new thermally stable synthetic oils based on hydrocarbon esters which do not have β-hydrogens in the alkoxy group.[2] Perfluorinated esters, which do not have hydrogen atoms to cause the above-mentioned intramolecular reactions, can also be considered to be thermally stable. In this Communication, we wish to report that certain perfluoroesters *do* decompose at elevated temperatures in a fashion quite different from hydrocarbon esters.

Currently, perfluoroesters have become important intermediates in the recent commercial technology to produce various perfluorocarboxylic acids in large quantities. The technology involves the direct fluorination of hydrocarbon esters in a liquid-phase fluorination system.[3−5] One of the most significant advantages of this technology is that very pure, isomer-free perfluoroesters, which are further hydrolyzed to perfluorocarboxylic acids, can be prepared in high yields.

Various perfluoroesters were prepared from corresponding hydrocarbon esters by the direct fluorination technique above. The perfluoroesters which were prepared are shown in Figure 1. The fluorination was carried out according to the previously published procedure,[5] and the obtained perfluoroesters were carefully purified by distillation under vacuum. Typically, the direct fluorination was carried out by slowly feeding a solution of approximately 5 g of appropriate hydrocarbon ester in 200 mL of 1,1,2-trichlorotrifluoroethane over 4 h into a reactor charged with 500 mL of 1,1,2-trichlorotrifluoroethane. Simultaneously, a 20% F₂/He gas mixture (500 mL/min) was fed into the reactor at 25 °C. In the case of perfluoroester **6**, 100 g of sodium fluoride powder was added to the reactor as a hydrogen fluoride scavenger to protect the ether linkages. The other perfluoroesters were obtained in good yields (>70%) without sodium fluoride.

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(1) Taylor, R. In *The Chemistry of Functional Groups, Supplement B, The Chemistry of Acid Derivatives*; Patai, S., Ed.; John Wiley & Sons: Chichester, UK, 1979; Part 2, Chapter 15.
(2) Randles, S. J. In *Synthetic Lubricants and High-Performance Functional Fluids*; Shubkin, R. L., Ed.; Chemical Industries 48; Marcel Dekker: New York, 1993; p 41.
(3) Lagow, R. J.; Margrave, J. L. *Prog. Inorg. Chem.* **1979**, *26*, 161.
(4) Lagow, R. J. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Howe-Grant, M., Ed.; John Wiley & Sons: New York, 1994; Vol. 11, p 482.
(5) Bierschenk, T. R.; Juhlke, T. J.; Kawa, H.; Lagow, R. J. U.S. Patent 5,093,432, 1992.
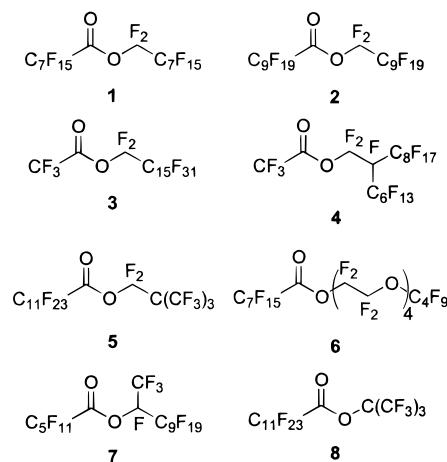

Figure 1. Prepared perfluoroesters.

Table 1. Conditions, Products, and Yields of the Decomposition Reaction of Perfluoroesters

ester	condition	product	yield (%)
1	232 °C, distill	$C_7F_{15}COF$	>95
2	254 °C, distill	$C_9F_{19}COF$	>95
3	252 °C, distill	CF_3COF	-[a]
		$C_{15}F_{31}COF$	>95
4	240 °C, distill	CF_3COF	-[a]
		$C_8F_{17}(C_6F_{13})FCOF$	>95
5	243 °C, distill	$C_{11}F_{23}COF$	70
		$C(CF_3)_3COF$	-[a]
6	250 °C, distill	$C_7F_{15}COF$	>95
		$C_4F_9O(CF_2CF_2O)_3CF_2COF$	>95
7	224 °C→182 °C reflux, 24 hr	$C_5F_{11}COF$	73
		$CF_3COC_9F_{19}$	73 [b]
8	235 °C reflux, 24 hr	recover **8**	

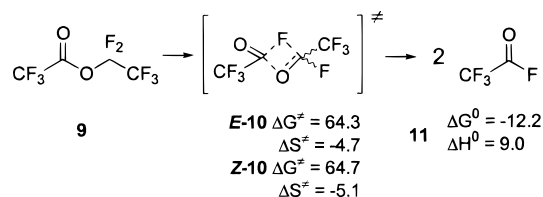[a] Yield not available. [b] Recover **7** (27%).

Perfluoroester **8** was also prepared from perfluorododecanoyl chloride and sodium perfluoro-*tert*-butoxide.[6]

The thermal decomposition was performed in a small Pyrex glass distillation apparatus under a dry argon atmosphere. Extreme care was taken to prevent the purified perfluoroesters from being exposed to moisture during the transfer to the apparatus. The reaction vessel was carefully heated using a heating mantle to allow the volatile products to distill out slowly.

The condition of the decomposition was found to depend on the number of fluorine atoms located at the α-position of the alkoxy group. The decomposition temperatures of the perfluoroesters are summarized in Table 1. All the perfluoroesters which had two fluorine atoms at the α-position (**1−6**) immediately decomposed over a narrow range of temperatures (232−254 °C). It these cases, the decomposition temperature does not depend very much on the size or the structure of the perfluoroester. Perfluoroester **7**, which has a branching at the α-position, slowly decomposed at 224 °C into perfluorohexanoyl fluoride and perfluoro-2-undecanone, while perfluoroester **8**, which has no fluorine atoms at the α-position, showed no signs of the decomposition after being refluxed (235 °C) for 24 h.

To explore this decomposition reaction further, AM1 semiempirical calculations[7] were performed using a very simplified model compound, perfluoro(ethyl acetate) (**9**), as shown in Scheme 1.

(6) De Pasquale, R. J. *J. Org. Chem.* **1973**, *38*, 3025.
(7) Dewer, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

Scheme 1[a]

9

E-10 $\Delta G^{\ddagger} = 64.3$
$\Delta S^{\ddagger} = -4.7$
Z-10 $\Delta G^{\ddagger} = 64.7$
$\Delta S^{\ddagger} = -5.1$

11 $\Delta G^0 = -12.2$
$\Delta H^0 = 9.0$

[a] Thermodynamic data are in kcal/mol at 498 K except $\Delta S^{\ddagger}$, which are in cal/mol·K at 498 K.
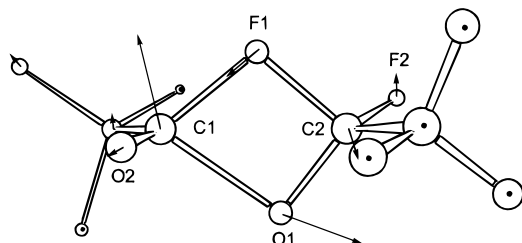

Figure 2. The structure of **E-10** with the vectors corresponding to imaginary frequency.

Four geometries for the reactant (**9**), two for the transition state (**E-10** and **Z-10**), and one for the product (**11**) were obtained respectively.[8] The free energy difference (ΔG°) indicates that the product is favored more than the reactant. On the other hand, the enthalpy difference (ΔH°) suggests that this reaction may be endothermic. The negative entropy of activation ($\Delta S^{\ddagger}$) values are consistent with the proposed cyclic transition state structure which involves the α-fluorine transfer. The high activation energy ($\Delta G^{\ddagger}$) values agree with the experimental results in that the reaction required a relatively large amount of heat energy. It should be noted that the activation energy values are lower than the one required to dissociate C−O bond (calculated to be 68.0 kcal/mol[9]).

The structure of **E-10** is shown in Figure 2. The obtained transition state structures are similar to that of the decomposition of hexafluorodimethyl ether which was proposed by Pacansky and Waltman.[10] The quadrilateral composed by C1−O1−C2−F1 is almost planar. The thermal mode vectors corresponding to the imaginary frequency indicate the exact path from the reactant to the products.

Selected partial atomic charges, bond lengths, and bond orders for the lowest energy structures of **9**, **E-10**, and **11** are summarized

(8) The AM1 calculations were performed using MOPAC 94: Stewart, J. J. P., Frank J. Seiler Research Laboratory, U.S. Air Force Academy, 1994. Geometries were obtained by the rigid search method and optimized by eigenvector following method within "PRECISE" mode. Optimized structures were further characterized by vibrational analysis. Transition state structures were confirmed to have only one imaginary frequency as required.
(9) The total of the free energy of trifluoroacetyl radical (CF3CO•) and pentafluoroethoxy radical (C2F5O•).
(10) Pacansky, J.; Waltman, R. J. *J. Fluorine Chem.* **1997**, *82*, 79.

Table 2. Selected Partial Atomic Charges, Bond Lengths, and Bond Orders

	9	E-10	11
	Charges		
C1	+0.282	+0.350	+0.301
O1	−0.304	−0.465	−0.220
O2	−0.225	−0.208	−0.220
C2	+0.367	+0.372	+0.301
F1	−0.117	−0.069	−0.087
F2	−0.117	−0.103	−0.087
	Bond Lengths (Å)		
C1−O1	1.369	1.812	∞
C1−O2	1.216	1.209	1.221
C2−O1	1.416	1.334	1.221
C2−F1	1.356	1.486	∞
C2−F2	1.356	1.348	1.333
C1−F1	2.779[a]	1.537	1.333
	Bond Orders		
C1−O1	0.970	0.386	
C1−O2	1.920	1.948	1.916
C2−O1	0.891	1.178	1.916
C2−F1	0.989	0.638	
C2−F2	0.989	1.006	1.019
C1−F1	0.002	0.499	1.019

[a] Atom distance.

in Table 2. These results indicated that all the bond changes at the C1−O1−C2−F1 quadrilateral proceed almost simultaneously. The electropositivity of C1 and electronegativity of O1 in the transition state increase more than those in the ground states, indicating the availability for bonding.

Thus, it is suspected that this reaction proceeds in a concerted fashion which involves the ionic-like dissociation of the C1−O1 bond and the intramolecular transfer of the α-fluorine. At elevated temperatures, the perfluoroesters vibrate vigorously enough to change their conformations to ones appropriate for the decomposition.

In summary, we have found a new thermal decomposition reaction of perfluoroesters. While the decomposition of hydrocarbon esters mentioned earlier involves an intramolecular migration of the β-hydrogen atom, the AM1 calculation results suggest that the decomposition of perfluoroesters proceeds with an intramolecular migration of the α-fluorine atom via the transition state **TS-2**.

TS-2

(2)

Supporting Information Available: Characterization data of **1−8** and the thermal decomposition products (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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