Journal of Fluorine Chemistry, 49 (1990) 217–224

Received: December 22, 1989; accepted: April 17, 1990

BROMO END-CAPPED PERFLUOROPOLYETHERS (*)

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SUMMARY

Light mediated heterolysis of perfluoropolyether polyperoxides in the presence of bromine effects the formation of bromo end-capped perfluoropolyethers. Yields are a function of starting material composition and reaction variables.
Under certain conditions relatively low molecular weight dibromo end-capped perfluoropolyethers are isolated in yields exceeding 70%. A reaction scheme is presented that is consistent with the observed experimental data.

INTRODUCTION

The photooxidation of tetrafluoroethylene [1] in solvent at low temperature leads to the formation of perfluoropolyether polyperoxide mixtures. Subsequent peroxide removal and end group stabilization afford chemically inert, neutral mixtures of oxytetrafluoroethylene/oxydifluoromethylene [2] perfluoropolyethers (PFPE) now commercialized under the tradename Fomblin Z Fluids.

(*) Paper presented in part at the 12th International Symposium on Fluorine Chemistry, August 1988, University of California Santa Cruz, U.S.A.

0022-1139/90/$3.50

The energetic polyperoxides besides being theoretically interesting intermediates [3] also show a degree of synthetic versatility. Under certain conditions the chemical induced reductive peroxide cleavage yields acids with functionality approaching two. The acids have been converted to a series of Fomblin Z derivatives [4, 5], e.g., diols, diesters, dinitriles, diisocyanates. Herein, we wish to report the preparation of bromine end-capped PFPE by direct treatment of the polyperoxides with bromine and light at different temperatures. Bromo substituted fluorocarbons useful as synthetic intermediates or in biological applications have been cited extensively in the literature [6].

EXPERIMENTAL

Molecular weights were determined by NMR from intensity comparison between end group and internal fluorines.

For neutral products of low molecular weight, determinations were checked by GPC [7]. ^{19}F NMR spectra were recorded on a Varian 200 spectrometer using $CFCl_3$ as an internal standard. Peroxide content of crude oils were measured by standard titration procedures. The obtained values compared favorably ($\pm$ 5%) with those calculated by the NMR method. The photochemical reactor was cylindrical, constructed of Pyrex, and stirred magnetically. The irradiation source, a Hanau TQ 150, 47 Watt lamp, was externally cooled and fitted into a double quartz well that was immersed in the reactant fluid.

Typical reaction procedure

The photochemical reactor was fitted with a reflux condenser, addition funnel, and blanketed in a nitrogen atmosphere.

A tetrafluoroethylene derived perfluoropolyether polyperoxide [8], 2942 g, MW > 100,000, peroxide content 2.0 g/100 g, 1.8 moles, (run 7, Table I), was charged to the reactor, degassed, magnetically stirred, and heated to 100°C. At this temperature, irradiation was commenced and bromine (400 g, 2.5 moles) was added dropwise at such a rate to maintain a slight color in solution and slow reflux. During the addition carbonyl fluoride was liberated and collected in a liquid oxygen trap (125 g total). The addition was complete after 148 hr. The reaction mixture was cooled to 60° and vacuum applied to remove excess Br_2 and low boilers (10 mm, 20 min).

The reaction mixture was cooled to 25°, weighed (2432 g), and sampled for NMR analysis and titration (see Table 1).

A 300 g sample of the above was washed with methanolic KOH (10% by weight 3 x 150 cc).

The bottom layer was dried ($MgSO_4$), filtered and weighed 272.2 g. The mixture was composed of a 95:5 ratio of dibromo to bromo-trifluoromethoxy perfluoropolyether (NMR) of 1400 MW.

The MeOH/KOH layer was acidified with aqueous HCl and the bottom layer separated, dried and weighed (13 g). NMR analysis indicated 1680 MW, and end-group ratio ($OCF_2Br:OCF_2CO_2H:OCF_3$ = 90:6:4).

A 122 g sample of the above dibromo fraction was molecularly distilled at reduced pressure (10^{-2} mm) to give a trap fraction, a distillate and bottoms.

Analyses of the fractions are according to the following table.

Fraction	g	Mwt (NMR)	Mwt (GPC)	mole % OCF_2Br	mole % OCF_3
Trap	22.4	705	650	95	5
Distillate	14.0	1180	1035	96.2	3.8
Bottoms	86.6	2110	2150	94	5

Distillate Anal. Calc. for $BrCF_2O(CF_2CF_2O)_{3.6}(CF_2O)_6CF_2Br$; C: 16.7, F: 53.0, Br: 14.7; Found C: 16.8, F: 53.5, Br: 14.2. MW 1090 (calc).

The mass spectra of these materials are fascinating and worthy of a separate study. Positive ion spectra show extensive degradative rearrangement and are of limited utility for structural characterization. The CI negative ion spectra (MS-Gc, HP 5589A, 80 EV) recorded for the trap sample, i.e., total ion then single ion reconstruction chromatograms, again show appreciable degradative

rearrangement. However, a dominant peak of M/e-CF_2Br (626) is detected which corresponds to the structure $BrCF_2O(CF_2CF_2O)_2(CF_2O)_3CF_2Br$.
Parent or fragment ions containing two Br substituents were not detected apparently due to the ease of CF_2Br fragmentation.

RESULTS AND DISCUSSION

The reaction is simple to perform and consists of irradiating a PFPE polyperoxide/Br_2 mixture with or without an inert solvent. Following conventional work-up, the bromo PFPE derivatives are obtained in yields ranging from 75-95%; carbonyl fluoride is the only by-product (Table I).

TABLE 1

Brominations Reactions [a]

	Wt final / Wt initial	T °C	Solvent [b]	MWt(i)	MWt(f)	Initial Peroxide (g/100 g)	% OCF_2Br	% OCF_3	% OCOF
1 [c]	0.78	100	–	60,000	1500	1.04	95	2	2
2 [d]	0.87	10	–	60,000	4500	1.04	61	19	19
3 [d]	0.88	10	70% wt	60,000	3000	1.04	72	14	14
4 [d]	0.93	100	–	35,000	730	2.2	96	2	2
5 [d]	0.77	90	–	1100	700	1.6	32	39	28
6 [d]	0.73	50	70% wt	2700	1300	0.7	50	24	25
7 [c]	0.83	100	–	>100,000	1422	2.0	91	3.4	5.2

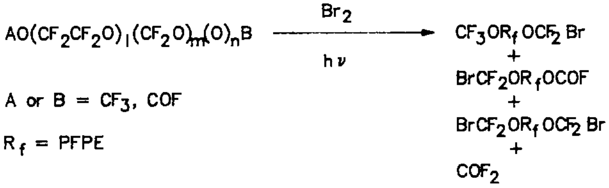
[a] Lamp—Hanau TQ 150, 47 w for λ = 2000—6000 Angstroms.
Bromine (molar excess over peroxide) added dropwise during reaction

[b] Galden (R) D 80, Tradename Montefluos

[c] 2 l reactor with a 4 cm optical path

[d] 0.3 l reactor with a 0.5 cm optical path

The progress of the reaction, disappearance of peroxide and appearance of $-OCF_2Br$ can be monitored by NMR. The rates of peroxide depletion are illustrated in Fig. 1. The yield, MWt, and composition of the bromo product distribution are a function of many interrelated variables, the most important being molecular weight and peroxide content of starting material.
Relevantly, the brominated end groups are exclusively $-OCF_2Br$. Several observations are worth brief elaboration based on the data presented in the table with the overall reaction represented by the following Scheme (I).



Scheme I.

The total bromide and in effect dibromide content in products can be controlled by the number of peroxide units (n) in the starting materials.

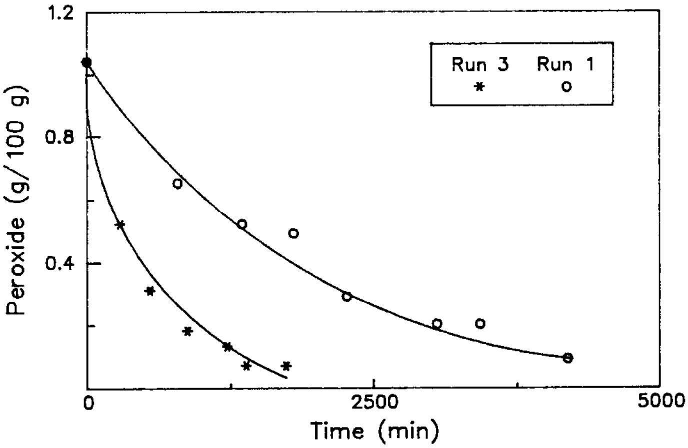
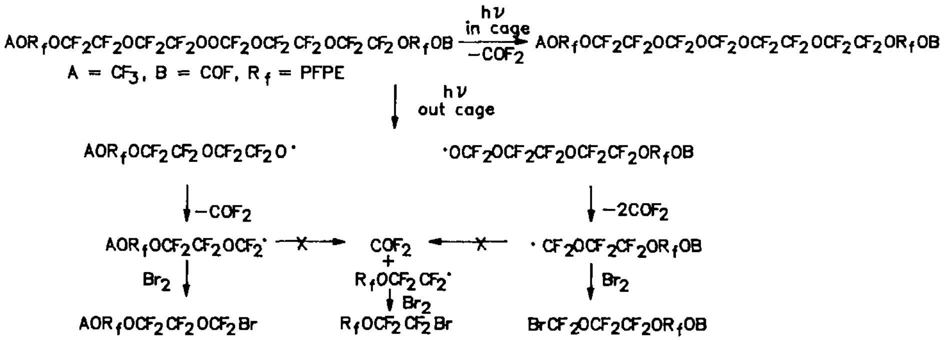


Fig. 1 . Rate of Peroxide consumption.

Higher yields of a variable range of molecular weight dibromides are obtained as n increases at constant molecular weight of starting material. This reflects a decrease in concentration of the initial (non-bromo) end groups in the polymer relative to the peroxy-links, the latter ultimately converted to the observed terminal bromo groups. At constant n, the higher the molecular weight of starting materials, the higher is the molecular weight range of products. Both peroxide content and molecular weight of starting material rely in a predictable way on the reaction conditions (flow rates, temperature, light intensity) of the initial tetrafluoroethylene photooxidation reaction.

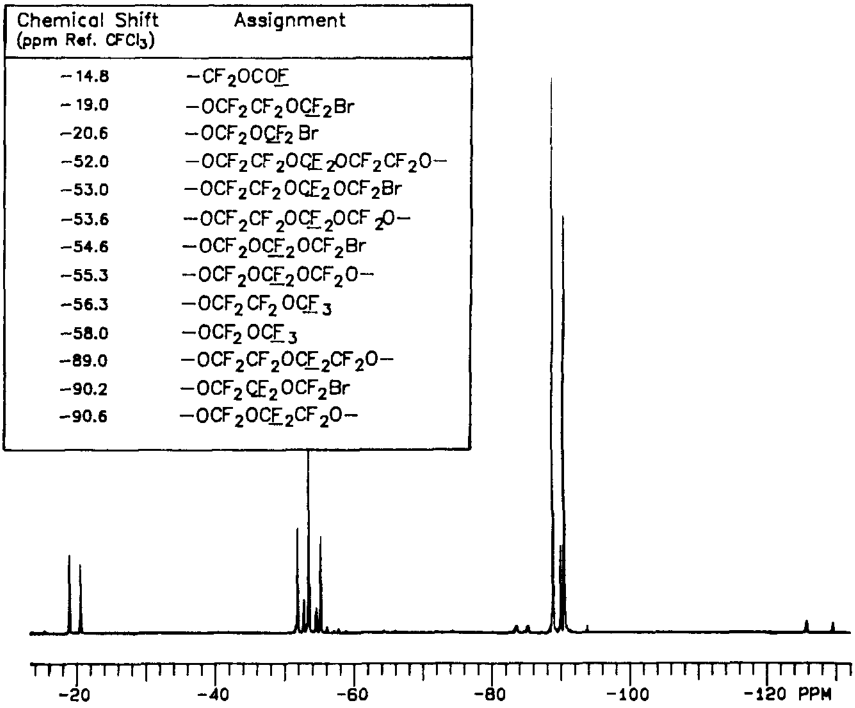
Temperature and viscosity have opposing effects on the bromination and influence the product distribution in the following manner. As temperature is increased or viscosity of the medium (added inert solvent) is decreased, the alkyletherdibromide yield increases. In contrast, as the peroxide content of the starting material decreases at constant molecular weight, mono bromide formation, i.e., bromo-trifluoromethoxy and bromo-fluoroformate mixtures are favored. These latter products can be maximized for example, by using a starting material where n=1 at low viscosity. Scheme II (n=1) is an interpretation of the reaction that takes into account the above observations.



Scheme II.

There are several features worthy of comment. Light absorption leads to peroxide fission affording alkoxy radicals [9]. Internal and external solvent cage effects are proposed in keeping with the observed viscosity and temperature product dependency. Loss of COF_2 through alkoxy radical β scission is common in these reactions and leads to R_fOCF_2 species [10].

The alkoxy difluoromethylene radicals, more stable than their alkoxy counterparts, are captured by Br_2 yielding products. Notably they do not undergo β scission with loss of COF_2 under the experimental conditions. Such an event would lead to the formation of $R_fOCF_2CF_2Br$ products which are undetected. For reference an NMR spectrum of a mixture of predominantly PFPE dibromides is shown in Fig. 2.



Chemical Shift (ppm Ref. $CFCl_3$)	Assignment
−14.8	$-CF_2OCO\underline{F}$
−19.0	$-OCF_2CF_2OC\underline{F}_2Br$
−20.6	$-OCF_2OC\underline{F}_2Br$
−52.0	$-OCF_2CF_2OC\underline{F}_2OCF_2CF_2O-$
−53.0	$-OCF_2CF_2OC\underline{F}_2OCF_2Br$
−53.6	$-OCF_2CF_2OC\underline{F}_2OCF_2O-$
−54.6	$-OCF_2OC\underline{F}_2OCF_2Br$
−55.3	$-OCF_2OC\underline{F}_2OCF_2O-$
−56.3	$-OCF_2CF_2OC\underline{F}_3$
−58.0	$-OCF_2OC\underline{F}_3$
−89.0	$-OCF_2CF_2OC\underline{F}_2CF_2O-$
−90.2	$-OCF_2C\underline{F}_2OCF_2Br$
−90.6	$-OCF_2OC\underline{F}_2CF_2O-$

Fig. 2. ^{19}F NMR of distilled dibromide.

ACKNOWLEDGEMENT

We gratefully acknowledge the contribution of Dr. Pianca and Ing. Morandi for the mass spectra and NMR analyses.

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2 The reactants and products described throughout this study contain a randomly distributed oxytetrafluoroethylene (CF_2CF_2O) and oxydifluoromethylene (CF_2O) units within the polymer backbone.

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