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THE ADDITION OF TETRAFLUOROETHYLENE OXIDE TO F-GLUTARYL FLUORIDE [1].
RELATIVE REACTIVITIES OF ACID FLUORIDES [2]

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SUMMARY

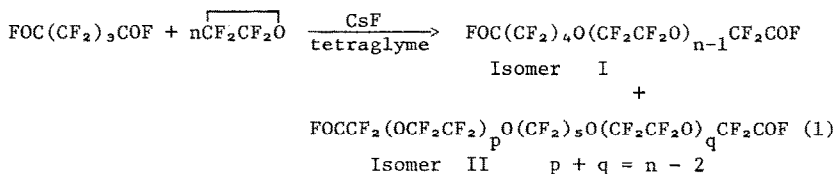
Data obtained from the addition of tetrafluoroethylene oxide to F-glutaryl fluoride show significant differences to exist between the relative reactivities of the acid fluoride groups involved. The order of reactivity is F-glutaryl fluoride > $-OCF_2COF$ > $-CF_2CF_2COF$.

INTRODUCTION

The addition of F-alkylene oxides to F-diacid fluorides provides a route to difunctional polyether intermediates suitable for a variety of applications requiring thermal and oxidative stability. As part of a program to prepare thermally stable triazine fluids and perfluoropolyether prepolymers, the addition of tetrafluoroethylene oxide (TFEO) to F-glutaryl fluoride (F-GF) was studied [3]. The data reported here provides a comparison of the relative reactivities of the acid fluoride groups involved in this reaction.

RESULTS AND DISCUSSION

Two types of isomers can result from the addition of TFEO to F-GF depending on whether addition occurs at one or both acid fluoride groups (equation 1).



The isomers may be distinguished by NMR spectroscopy by virtue of differences in chemical shifts of the two types of acid fluoride groups. NMR spectral data of a typical oligomer containing the two types of isomers are shown in Table 3. For oligomers where $n > 5$ the isomer ratio was established by NMR. For oligomers where $n = 2-5$ the two types of isomers were well resolved by GLC.

The reaction was studied in detail by analyzing samples withdrawn from the reaction mixture as the TFEO was added. The results are given in Table 1. The vertical columns represent the composition of the reaction mixture after the designated amount of TFEO had been added.

It will be seen from the data that the TFEO reacts preferentially with the F-GF before it reacts with the 1:1 adduct. Extrapolation of the data shows that at the addition of 1.0 moles of TFEO the 1:1 adduct accounts for over 90% of the reaction mixture. Continued addition of TFEO produces significant amounts of the 2:1 adduct only after all the F-GF has reacted. However, addition of TFEO to the 1:1 adduct occurs preferentially at the end already substituted to form predominantly the unsymmetrical 2:1 adduct, ($n=2$, isomer I). The small amount of symmetrical 2:1 adduct ($n=2$, isomer II) which is formed reacts much faster than isomer I to the extent that it is no longer detected in the reaction mixture once the precursor ($n=1$, isomer I) has been totally consumed. The same fate occurs with the 3:1 and 4:1 adducts. With the 5:1 adduct the isomer II now predominates although it too reacts faster than isomer I as is shown by the increasing isomer ratio. The two isomers are no longer resolved on GLC for the oligomers containing more than five units of TFEO.

A second oligomerization was carried out on larger scale to give an oligomeric mixture ranging from the 4:1 to 9:1 adducts. After isolation of the pure oligomers by fractionation, NMR was used to determine the isomer ratio. As seen from Table II, the isomer ratio changes dramatically from pure isomer I in the 5:1 adduct to pure isomer II in the 9:1 adduct.

A detailed discussion of the polymerization of F-alkylene oxides appears in the literature [4]. The principal reactions involved are shown in the following equations.

TABLE I
Product distribution during the addition of TFEO to F-GF (Lower molecular weight range)

n	Isomer	Mole Ratio TFEO:F-GF													
		0.8	1.2	1.9	3.0	3.5	4.3	5.3	6.4	7.5					
0	(PFGF)	19.9	4.6	--	--	--	--	--	--	--	--	--	--	--	--
1	I	77.0	83.7	37.5	3.3	1.1	--	--	--	--	--	--	--	--	--
2	I	1.0	5.8	46.2	69.3	50.2	4.9	1.2	--	--	--	--	--	--	--
2	II	--	0.6	2.3	--	--	--	--	--	--	--	--	--	--	--
3	I	--	0.5	4.8	27.4	42.2	34.8	21.6	5.7	0.8	--	--	--	--	--
3	II	--	--	0.5	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
4	I	--	--	--	--	trace	17.1	17.7	22.3	6.6	--	--	--	--	--
4	II	--	--	--	--	--	13.9	9.3	trace	--	--	--	--	--	--
5	I	--	--	--	--	--	2.4	3.4	10.8	13.9	--	--	--	--	--
5	II	--	--	--	--	--	13.7	14.9	15.8	3.5	--	--	--	--	--
6*	I & II	--	--	--	--	--	2.9	3.9	24.3	34.0	--	--	--	--	--
7*	I & II	--	--	--	--	--	--	0.1	5.7	30.1	--	--	--	--	--
8*	I & II	--	--	--	--	--	--	--	0.4	4.7	--	--	--	--	--

* Isomers were not resolved by GLC.

TABLE 2

Product distribution from the addition of TFEO to F-GF (Higher molecular weight range)

n	Wt % by GLC	bp°C/mm Hg	Isomer Ratio by NMR	
			I	II
4	2.3	--	--	--
5	13.5	107/11	>98	Not observed
6	15.6	86/0.3	90	10
7*	23.3	96/0.2	17	83
8	33.1	106/0.6	2	98
9	8.3	125/1.0	Not observed	>98

*NMR spectrum of this fraction given in Table 3.

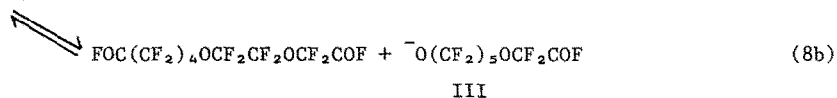
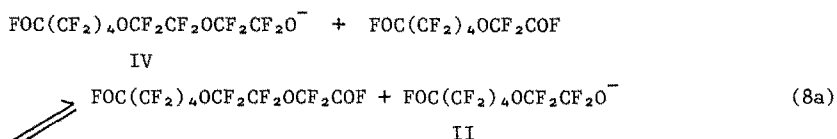
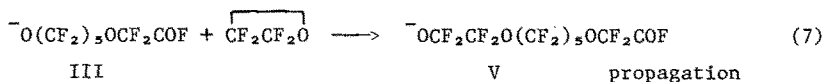
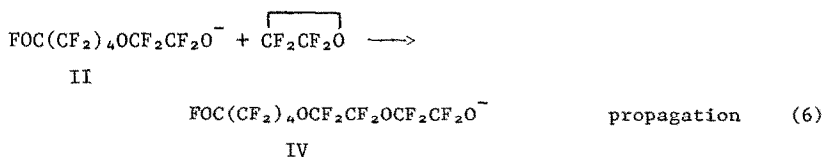
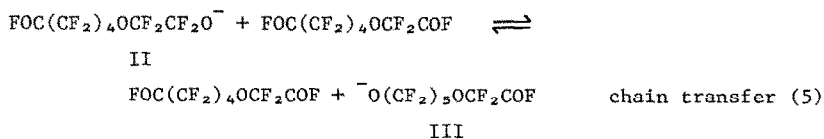
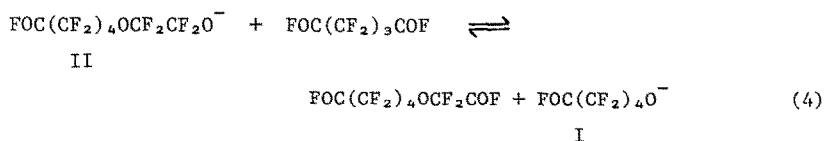
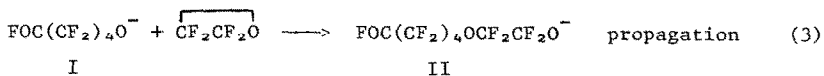
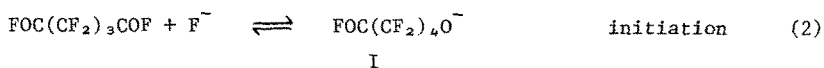
TABLE 3

F¹⁹ NMR spectral data of oligomer n = 7 (Table 2)

$\begin{array}{cccccccc} \text{AF} & \text{H} & \text{I} & \text{D} & \text{E} & \text{E} & \text{C} & \text{B} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \text{FOCCF}_2 & \text{CF}_2 & \text{CF}_2 & \text{CF}_2 & \text{CF}_2 & \text{O} & (\text{CF}_2 & \text{CF}_2 & \text{O})_6 & \text{CF}_2 & \text{COF} \end{array}$	1 part
$\begin{array}{cccccccccccc} \text{BC} & \text{E} & \text{E} & & \text{D} & \text{I} & \text{G} & \text{I} & \text{D} & & \text{E} & \text{E} & & \text{C} & \text{B} \\ \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & & \vdots & \vdots \\ \text{FOCCF}_2 & (\text{OCF}_2 & \text{CF}_2) & & \text{OCF}_2 & \text{CF}_2 & \text{CF}_2 & \text{CF}_2 & \text{CF}_2 & \text{O} & (\text{CF}_2 & \text{CF}_2 & \text{O}) & & \text{CF}_2 & \text{COF} \\ & & \text{m} & & & & & & & & & & & \text{n} & & \end{array}$	5 parts

Designation	Chemical Shift*	Pattern	Relative Area
A	-99.7	Multiplet	7
B	-88.95	Singlet	73
C	+0.7	Triplet by 11.5, doublet by 3, plus smaller multiplet	147
D	+6.9	Pentet by 10	150
E	12.3	Two overlapping multiplets	890
F	42.1	Quartet by 8	13
G	45.7	Pentet by 10	70
H	46.4	Pentet by 10	14
I	49.1	Multiplet	145

* From CF₃COOH external reference.



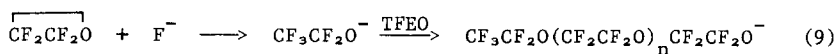
Initiation is by formation of the alkoxide from F-GF and the cesium fluoride catalyst followed by reaction of this alkoxide with a molecule of TFEO to give the 1:1 alkoxide II. In order to account for the observed results chain transfer reaction (4) involving a fluoride ion transfer from alkoxide II to unreacted F-GF followed by chain propagation reaction (3) must occur more rapidly than the chain transfer reaction (5) and propagation reactions (6) and (7). Only when all the F-GF has reacted does further

propagation occur to any significant extent to form the 2:1 alkoxide IV by reaction (6). Chain transfer now occurs by transfer of fluoride ion from the 2:1 alkoxide IV to the 1:1 acid fluoride to form either alkoxide II or alkoxide III, reactions (8a), (8b). Again, to account for the observed product distribution, the alkoxide II must react with TFEO significantly faster than does alkoxide III. This shows that the acid fluoride group with an oxygen atom in the β position in the 1:1 adduct is more reactive than the acid fluoride group attached to the $-\text{CF}_2\text{CF}_2-$ group. The increased reactivity of this particular acid fluoride group is also shown by the higher adducts and explains the relatively short-lived appearance during the early stages of the reaction of the type II isomers which contain two of the more reactive groups. In addition it accounts for the preponderance of the type II isomers in the higher molecular weight products of the distribution curve as these are present solely as the reaction products of the faster reacting type II isomers. The distribution curve for this particular reaction can consequently be divided into three zones. Low molecular weight products will be type I isomers, high molecular weight products type II isomers and intermediate molecular weight products will be mixtures.

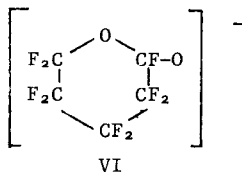
The greater reactivity of the $-\text{OCF}_2\text{COF}$ group compared to the $-\text{CF}_2\text{CF}_2\text{COF}$ group in the adducts of $\underline{\text{F}}\text{-GF}$ and TFEO would lead to the prediction that $\underline{\text{F}}\text{-GF}$ itself, containing two of the lesser reactive groups, would be less reactive than the 1:1 and higher adducts, and that as TFEO was added it would react preferentially with the adducts leaving unreacted $\underline{\text{F}}\text{-GF}$ and giving a wide distribution of products. The results, however, show that the reverse is true and that $\underline{\text{F}}\text{-GF}$ acid fluoride groups are even more reactive than the $-\text{OCF}_2\text{COF}$ groups.

The high reactivity of $\underline{\text{F}}\text{-GF}$ may be unique among the perfluorinated diacid fluorides. It has been reported [5] that addition of TFEO to $\underline{\text{F}}\text{-malonyl fluoride}$ ($\underline{\text{F}}\text{-MF}$) and to $\underline{\text{F}}\text{-adipyl fluoride}$ ($\underline{\text{F}}\text{-AF}$) resulted in 20% unreacted $\underline{\text{F}}\text{-AF}$ in the latter reaction product. In both reactions significant amounts of TFEO homo-oligomers were formed. This is in contrast to the work reported here where essentially no homo-oligomers of TFEO were produced.

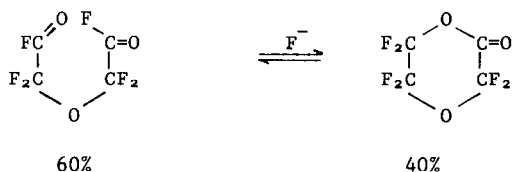
The higher reactivity of $\underline{\text{F}}\text{-GF}$ and the absence of TFEO homo-oligomers can be explained if the equilibrium reaction (2) lies strongly to the right side, thereby removing free fluoride ion from the system and preventing fluoride ion-catalyzed oligomerization of TFEO, reaction (9).



Possible stabilization of the alkoxide of $\underline{\text{F}}$ -GF [I] may be due to a cyclic transition state VI. Addition products from this lactone have not



been isolated possibly because the lack of flexibility of the $-(\text{CF}_2)_3-$ segment prevents complete cyclization. The lactone from $\underline{\text{F}}$ -oxydiacetyl fluoride, however, with the greater flexibility derived from the ether linkage has been isolated and found to be in equilibrium with the parent diacid fluoride [6].



EXPERIMENTAL

F^{19} NMR spectra were recorded on a Varian XL 100 instrument at 94.1 MHz. GLC analyses were obtained using a 6 ft. Fomblin XR/75, 15% on HMDS-treated gaschrom GL, programmed from 40°C to 200°C at 15°/min. TFEO was prepared by the bromine-sensitized photochemical oxidation of tetrafluoroethylene [7]. Throughout the experiment the TFEO cylinder was kept below -60°C in a cooling bath to prevent rearrangement to CF_3COF and possible explosive decomposition [4].

$\underline{\text{F}}$ -GF (72 g) was added to pre-dried cesium fluoride (3.0 g) in tetraethyleneglycol dimethyl ether (50 ml) in a flask equipped with a magnetic stirrer, thermowell, septum cap and a connection to a vacuum manifold. The contents of the flask were stirred at 45°C for 2 hr then cooled to -30°C when the air was pumped off. The system was then charged to 300 mm pressure with TFEO and maintained at this pressure with a regulating valve. Reaction temperature was maintained at -5 to +5°C. Samples of the lower fluorocarbon

layer were withdrawn throughout the reaction, according to Table 1, using a syringe so that the reaction flask was not opened to the atmosphere. A total of 258 g TFE0 were added in this manner.

The above reaction was repeated using F-GF (450 g, 1.84 moles), cesium fluoride (10 g), tetraethyleneglycol dimethyl ether (200 ml) and TFE0 (1537 g, 13.25 moles) to give the oligomeric mixture (1987 g) described in Table 2. Fractional distillation was carried out on a four-foot Oldershaw column.

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REFERENCES

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