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# AEROSOL DIRECT FLUORINATION: DIRECT SYNTHESIS OF PERFLUORINATED GLYME ETHERS

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## SUMMARY

Aerosol direct fluorination of 1,2-dimethoxyethane, bis(2-methoxyethyl) ether, triethyleneglycol dimethyl ether, and tetraethyleneglycol dimethyl ether produced the perfluorinated analogs in 36%, 22%, 30% and 15% isolated yields based on total input of hydrocarbon into the reactor. High effluent concentrations in excess of 80% were obtained in all cases indicating that low yields are primarily due to mechanical losses, not fragmentation or incomplete reaction. The clean reaction and the ability to produce high molecular weight fluorocarbons by direct fluorination suggests the applicability of aerosol fluorination to the production of fluorinated fluids and oils.

## INTRODUCTION

Perfluorinated polyethers have unusual properties which make them likely candidates for industrial purposes. They exhibit very good chemical and thermal stability and may be used for solvents and lubricants[1]. Previous synthesis of perfluoro glymes by various methods have produced perfluoroglyme, -diglyme, -triglyme and -tetraglyme. The first reported synthesis of perfluoroglyme was by Simons[2] in 1950 by electrolyzing 1,4-dioxane in liquid HF. Direct fluorination of 1,2-dimethoxyethane and bis-2-methoxyethyl ether

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has been done previously to give perfluorinated products employing the modified LaMar technique [3]. However this was a batch process and gave yields of 21% and 16% respectively of a complex mixture. Later perfluorodimethoxyethane was synthesized by degradation of perfluoro-1,4-dioxane which had been produced from electrochemical fluorination [4], but this was not the desired product and no yield was reported. The first synthesis of perfluorotriglyme and tetraglyme as well as pentaglyme was carried out by Gerhardt and Lagow [5,6]. However these were all contained in a complex mixture of products from the direct fluorination of polyethylene oxide. Again the reported yields were only 0.66, 0.66, and 0.68% respectively and the batch process was employed making it a less desirable process for industrial application.

## EXPERIMENTAL

The basic description and explanation of functions of the aerosol fluorinator has been previously described [7]. A modification to this system was made to better control a homogeneous input of hydrocarbon [8]. Product workup after HF removal consists of vacuum line fractionation, infrared assay of fractions; separation of constituents by gas chromatography utilizing either a 7m x 3/8 inch 13% fluorosilicone QF-1 (Analabs) stationary phase on 60-80-mesh, acid-washed, Chromosorb P conditioned at 255°C (12h) or a 4m x 3/8 inch 10% SE-52 phenyl methyl silicone rubber on acid-washed 60-80-mesh chromosorb P conditioned at 250°C (12h). Significant products were collected from gas chromatographic separation (Bendix Model 2300, subambient multicontroller), transferred back to the vacuum line, then assayed and characterized by vapor-phase infrared spectrophotometry, PE1330, electron-impact (70eV) and chemical-ionization ($CH_4$ plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 MS, 5934A computer), and $^1H$ and $^{19}F$ nuclear magnetic resonance (JOEL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. Mass spectrometry gave similar results for perfluorinated triglyme and perfluorinated tetraglyme. Major mass spectra peaks correspond to $CF_3$ and $CF_3O$.

### Aerosol Fluorination of 1,2-dimethoxyethane

Glyme (Aldrich; 99+%) was used as received. Details of the aerosol fluorination parameters are given as reaction 1. A 4h, photochemically finished run of 2.29g of crude product was transferred to the vacuum line and fractionated into -78, -131 and -196°C fractions. An infrared assay of the -196°C fraction showed perfluorinated fragments and was discarded. The -78 and -131°C fractions were combined and separated gas chromatographically on the SE-52 column (25°C/10 s, 2°C/m), producing F-1,2-dimethoxyethane (98% effluent purity, Table I), a 36% yield based on total input.

### Aerosol Fluorination of bis-2-methoxyethyl ether

Diglyme (Aldrich 99%) was used as received. Details of fluorination parameters are given as reaction 2 in Table I. A 4h, photochemically finished run of 1.60g of crude product was transferred to the vacuum line and fractionated into -45, -78 and -196°C fractions. An infrared assay of the -196°C fraction showed perfluorinated fragments and was discarded. The -45 and -78°C fractions were combined and separated gas chromatographically on the SE-52 column (25°C/10 s, 2°C/m), producing F-bis-2-methoxyethyl ether (89% effluent purity, Table I), a 22% yield based on total input.

### Aerosol Fluorination of Triethylene glycol dimethyl ether

Triglyme (Aldrich 99%) was used as received. Details of the aerosol fluorination parameters are given as reaction 3 in Table I. A 4h, photochemically finished run of 1.16g of crude product was transferred to the vacuum line and fractionated into -78, and -196°C fractions with the -196°C fraction being discarded because infrared assay showed it to be perfluorinated fragments. The -78°C fraction was separated gas chromatographically on

TABLE I. Typical Aerosol Fluorination Reaction Parameters

| Reaction number | Starting Compound | Fluorine Flow mL/min |  |  | Helium Diluent mL/min |  |  | Reaction Temp, °C |  |  | Main Helium Carrier mL/m |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | mod 1[a] | mod 2 | mod 3 | mod 1 | mod 2 | mod 3 | mod 1 | mod 2 | mod 3 |  |
| 1 | 1,2-dimethoxyethane | 20 | 20 | 14 | 140 | 130 | 150 | -40 | -30 | 0 | 500 |
| 2 | bis-2-methoxyethyl ether | 20 | 20 | 18 | 140 | 130 | 150 | -40 | -30 | 0 | 500 |
| 3 | triethylene glycol dimethyl ether | 20 | 20 | 35 | 140 | 130 | 150 | -40 | -30 | 0 | 500 |
| 4 | triethylene glycol dimethyl ether[b] | 20 | 20 | 35 | 140 | 130 | 150 | -20 | -10 | 0 | 500 |
| 5 | tetraethylene glycol dimethyl ether | 20 | 20 | 35 | 140 | 130 | 150 | -40 | -30 | 0 | 500 |

| Reaction number | Hydrocarbon Throughput mmol/h | Primary Helium Carrier mL/min | Second. helium carrier mL/min | Overall Stoichiometry hc:$F_2$ | Reaction Effluent Purity % of product | Product Yield % total input |
|---|---|---|---|---|---|---|
| 1 | 4.83 | 450 | 50 | 1:30 | 98 | 36 |
| 2 | 3.50 | 450 | 50 | 1:44 | 89 | 22 |
| 3 | 2.77 | 450 | 50 | 1:72 | 92 | 20 |
| 4 | 2.77 | 450 | 50 | 1:72 | 81 | 30 |
| 5 | 2.28 | 450 | 50 | 1:88 | 94 | 15 |

[a] Reactor staging module

[b] Different run

the SE-52 column (25°C/10 s, 2°C/m), producing F-triethylene glycol dimethyl ether (92% effluent purity, Table I), a 20% yield based on theoretical throughput. A second run (reaction 4) was made using the same parameters except at warmer temperatures. The effluent purity of product decreased to 81%, however a 30% yield was achieved based on total input.

### Aerosol Fluorination of Tetraethylene glycol dimethyl ether

Tetraglyme (Aldrich, 99+%) was used as received. Details of the aerosol fluorination parameters are given as reaction 5 in Table I. A 4h, photochemically finished run of 1.02g of crude product was transferred to the vacuum line and fractionated into -45, and -196°C fractions. An infrared assay of the -196°C fraction showed perfluorinated fragments and was discarded. The -45°C fraction was separated gas chromatographically on the SE-52 column (25°C/10 s, 2°C/m), producing F-tetraethylene glycol dimethyl ether (94% effluent purity, Table I), a 15% yield based on total input.

## RESULTS AND DISCUSSION

In the past synthesis of perfluorinated glymes used their respective hydrocarbon analogs as starting material only for perfluorinated glyme and diglyme. The aerosol fluorination synthesis gives higher yields and uses the hydrocarbon precursors as starting material in all cases. Since this process is a flow system and not a batch process, industrial application is more practical. The synthesis of the higher molecular weight glymes is significant in that much higher yields are obtainable by aerosol direct fluorination than other methods used previously. The lowest yield of the subject compounds was 15% based on theoretical throughput. However this is somewhat misleading since product effluent purity was still 94% in this case. Several runs were made on these compounds with the express intent of determining where losses occur. The more hydrocarbon that was injected into the system (longer run) actually increased the overall theoretical yield. Therefore a fixed volume loss must be overcome before the system begins to operate more efficiently. Additionally the flash evaporator gained as much as 30% weight of injected hydrocarbon weight during a run, hence only 70% of the hydrocarbon ether was actually delivered which deflates yields based on input significantly. Other losses due to oil formation occurred in the photochemical cell due to inefficient cooling. Also products tended to condense on the reactor walls in the early stages of the reactor probably due to improper focusing of the streams. Therefore, the immediate problem becomes one of engineering improvements rather than chemical problems. Currently, modifications are being made to this system which hopefully will enhance theoretical yields to approach that of distribution yields based on an effluent concentration of product.

Also significant is the fact that these compounds are of higher molecular weights than any previously synthesized by the aerosol direct fluorination technique. In the case of tetraglyme the molecular weight of the hydrocarbon starting material is 222g/m while the perfluorinated product is 618g/m. This shows that the aerosol fluorination process is adaptable to the low volatility oils and thus is a feasible process with regard to the perfluorination of polymers from their analogs. While extensive, sometimes violent fragmentation is usually the result of most direct fluorination procedures, the aerosol direct fluorination method takes advantage of effective heat dissipation of the heat of reaction which significantly decreases fragmentation. Since it is a flow system this makes it possible to increase the scale for the manufacture of materials in large quantities.

In each reaction the desired perfluoro product was the major product, in high effluent concentration (purity). Characterization of perfluorinated glyme and perfluorinated diglyme was carried out by infrared analysis and

TABLE II

$^{19}F$ NMR and IR ($cm^{-1}$) data of perfluorinated triglyme and tetraglyme

| | A | B | C | $J_{ac}$ |
|---|---|---|---|---|
| $\underset{A}{CF_3}-O-\underset{C}{CF_2}-\underbrace{CF_2-O-CF_2-O-CF_2}_{B}O-CF_2-O-CF_3$ | -55.93ppm(t) | -89.27ppm(s) | -91.31ppm(d) | 9.16 Hz |
| | Relative Integrals A:B:C = 3:4:2 | | | |
| | IR: 685(w), 738(m), 790(w), 905(m), 1140(s), 1160(s), 1200(s), 1230(s), 1245(s), 1290(s) | | | |
| | A | B | C | $J_{ac}$ |
| $\underset{A}{CF_3}-O-\underset{C}{CF_2}-\underbrace{CF_2-O-CF_2-CF_2-O-CF_2-CF_2-O-CF_2}_{B}-CF_2-O-CF_3$ | -55.97ppm(t) | -89. 34ppm(s) | -91.35ppm(d) | 9.16 Hz |
| | Relative Integrals A:B:C = 3:6:2 | | | |
| | IR: 685(w), 725(m), 765(m), 910(m), 1130(s), 1160(s), 1195(s), 1235(s), 1245(s), 1295(s) | | | |

agreed exactly with previous literature values [3]. However, characterization of perfluorinated triglyme and perfluorinated tetraglyme gave some discrepancy to previous literature nmr values [5,6]. Only the infrared fingerprint region of perfluorinated triglyme and perfluorinated tetraglyme have been previously reported, which are in agreement with our results. Table II gives the details of the complete infrared findings, as well as other characterization details of perfluorinated triglyme and perfluorinated tetraglyme.

## ACKNOWLEDGEMENT

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