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THERMAL DECOMPOSITION OF PERFLUOROALKANESULFONYL FLUORIDES: THE PYROLYSIS OF PERFLUORO-*n*-OCTANE-1-SULFONYL FLUORIDE

M. NAPOLI, C. FRACCARO, A. SCIPIONI and R. ARMELLI

Institue of Industrial Chemistry, University of Padua, via
Marzolo, 9, 35100, Padua (Italy)

M. PIANCA

Montefluos C.R.S., via Bonfadini 148, 20138, Milano (Italy)

SUMMARY

The preliminary data obtained from thermal decompositions of perfluoro-*n*-octane-1-sulfonyl fluoride in a continuous tubular-flow reactor are reported. The pyrolysis results in a radical reaction producing fluorocarbons, with high conversions and with yields depending on the experimental conditions. The reaction mixture composition also depends on the experimental conditions, so it is possible to obtain a prevalent formation of either light or heavy fluorocarbons.

INTRODUCTION

Continuing our research on the chemical preparation of perfluorinated compounds suitable as artificial blood [1,2], a study on the thermal decomposition of perfluoroalkanesulfonyl fluorides has begun. In this paper are reported the preliminary data obtained from several experiments carried out using perfluoro-*n*-octane-1-sulfonyl fluoride (PFOSF) as starting material, in order to develop a process for other compounds more suitable for the artificial blood.

EXPERIMENTAL

A continuous tubular-flow iron reactor, containing copper chips and located in a furnace equipped with an automatic temperature control, has been used for the experiments. The void volume in the reaction zone, measured by benzene displacement, was 34 ml; this value has been used in order to calculate the mean residence time of the molecule in the reaction zone.

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The reactant was fed by a metering pump at various flow rates and was vaporized before going in the reactor. The reaction products were collected by cooling the vapours coming out of the reactor at 0-2 °C: in these first experiments the compounds not condensed were ignored (however, SO_2 and SO_2F_2 have been found in the gaseous phase). During the process the temperature was kept ± 1.5 °C of the stated value.

The collected reaction mixture (from now onwards named 'crop') was always a slurry. Then it was subdivided into two fractions by distillation before the GLC analysis; the liquid fraction was analysed directly, while the solid one was analysed after dissolution in freon 113. The operating conditions of the GLC analysis are reported in Table 1.

The 'crop' contained always many compounds, besides various amounts of unreacted PFOSF. The main ones of these compounds were identified as fluorocarbons by MS analysis; the mass spectral fragmentation pattern in each case contained the corresponding parent ion and the peaks (M-F) and ($M-CF_3$), besides the following major fragments: m/e 331 (C_7F_{13}), 319 (C_6F_{13}), 281 (C_6F_{11}), 269 (C_5F_{11}), 231 (C_5F_9), 219 (C_4F_9), 181 (C_4F_7), 169 (C_3F_7), 131 (C_3F_5), 119 (C_2F_5), 81 (C_2F_3) and the base peak 69 (CF_3).

The following remarks suggest a straight chain for the identified compounds:

- the ^{19}F NMR spectra of the 'crop', recorded after a hundred scans, showed a quite negligible signal for CF group (118 ppm from TFA ext.);
- the GLC retention times observed on the conditions of Table 1 for n-C_8F_{18}, n-$C_{12}F_{26}$ and n-$C_{16}F_{34}$ (synthesised from n-C_4F_9I, n-$C_6F_{13}I$ and n-$C_8F_{17}I$ respectively) were the same as the ones correspondingly observed for C_8, C_{12} and C_{16}; it can be supposed that also the other identified compounds have straight chains.

The operating conditions of the experiments are reported in Table 2, with the calculated values for the conversion, for the 'crop' yield (based upon the reactant fed) and for the fluorocarbon yields based upon either fed or converted reactant. These values have been calculated by the GLC quantitative data obtained by the normalization method, using a test mixture of synthetic n-C_8F_{18} (b.p. 104 °C), n-$C_{12}F_{26}$ (m.p. 75 °C) and n-$C_{16}F_{34}$ (m.p. 126 °C) under the assumption that the mean value of the correction factors obtained for n-C_8F_{18} and n-$C_{16}F_{34}$ relative to n-$C_{12}F_{26}$ may be used for all the components of the analyzed mixtures.

RESULTS AND DISCUSSION

Very high conversions result from Table 2, especially at the highest temperatures, while the fluorocarbon yields are much lower, also because these latter values have been calculated without considering that the reaction occurs with a loss of weight.

TABLE 1 Operating conditions of GLC analysis

Instrument: Perkin Elmer 'Sigma 3'.
Column: stainless steel filled with 5 wt. % SE-30 on 80/100 mesh Chromosorb P.
Carrier gas: He (20cc/min).
Detector: HVD at 250 °C.
Injector temperature: 250 °C.
Column temperature: 50 °C for 10 minutes, 6 °C/min till 200 °C, 200 °C for 10 minutes.

TABLE 2 Experimental conditions fixed on for the pyrolysis and calculated values of the conversion and of the yields

flow rate (kg/hr)	temperature (°C)	PFOSF fed (g)	PFOSF unreacted (g)	reaction mixture collected (g)	reaction mixture collected (% yield)	conversion (%)	% fluorocarbon yields based upon PFOSF fed	% fluorocarbon yields based upon PFOSF converted
0.7	460	416	173	321	77.2	58.4	35.5	60.9
	492	712	70	442	62.0	90.2	52.2	57.9
	520	527	22	273	51.8	95.8	47.6	49.7
	550	475	12	218	45.9	97.5	43.4	44.5
0.4	460	462	171	344	74.4	62.9	37.4	59.4
	492	465	42	287	61.7	91.0	52.7	57.9
	520	456	21	246	53.9	95.4	49.3	51.7
	550	292	8	145	49.6	97.3	46.9	48.2
0.2	460	198	18	131	66.2	90.9	57.1	62.8
	492	190	6	113	59.5	96.8	56.3	58.1
	520	185	5	101	54.6	97.3	51.9	53.3
	550	165	4	89	53.9	97.6	51.5	52.8

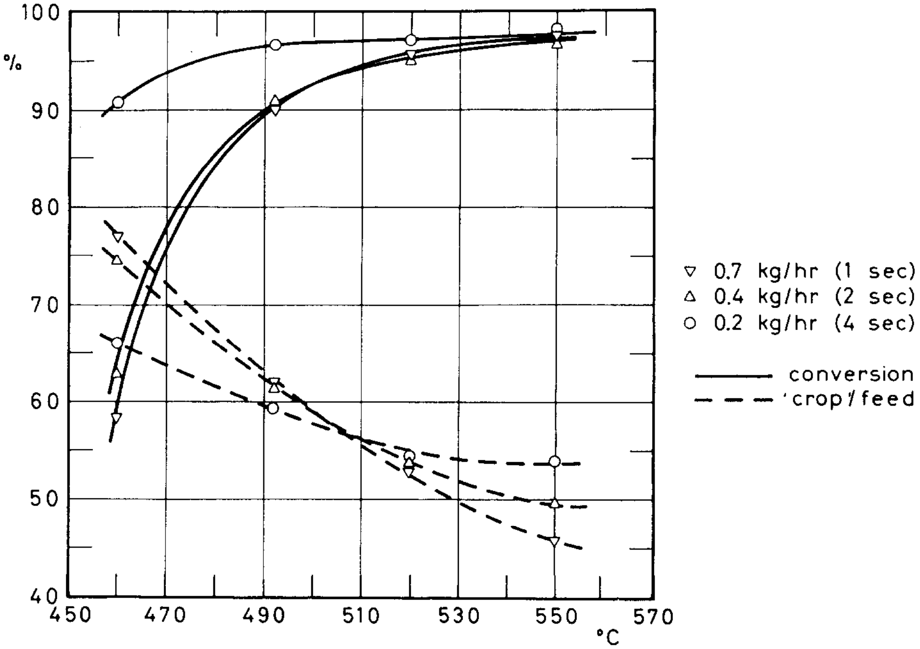

Fig. 1 Conversion and 'crop' yield plotted against temperature.

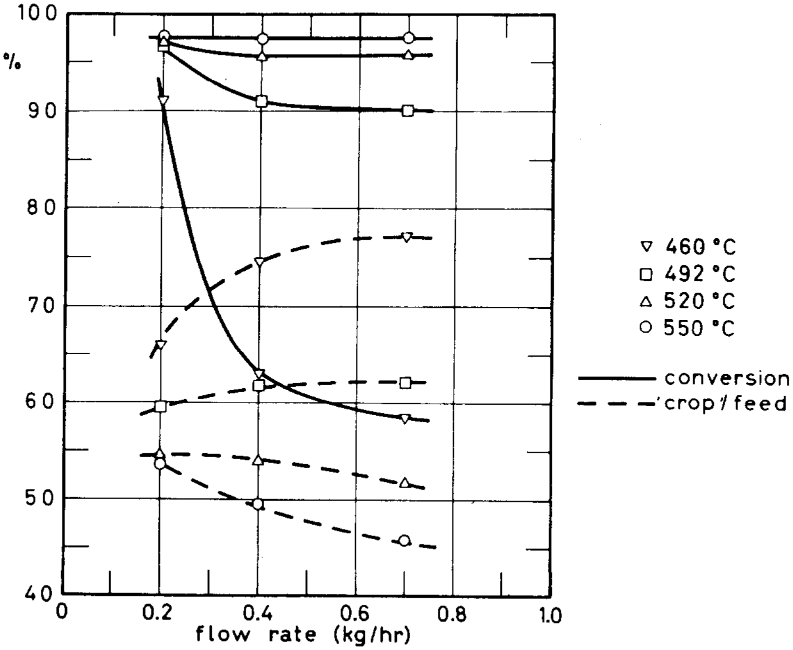

Fig. 2. Conversion and 'crop' yield plotted against flow rate.

The values of the conversion and of the 'crop' yield are plotted against temperature in Figure 1 for each flow rate used (also the corresponding mean residence times are reported), while in Figure 2 the same values are reported versus flow rate at the different temperatures used. The conversion always increases with temperature to a maximum value which is almost independent of the flow rate; it also changes with flow rate in a manner which depends on the temperature used: at low temperatures it is necessary to operate at low flow rates in order to obtain yields higher than 90 %, while at high temperatures high conversions have been obtained even with high flow rates.

The 'crop' yield, instead, drops as the temperature increases. This behaviour can be explained supposing that the 'crop' yield depends on different factors according to the temperature. At low temperatures it depends on the conversion: with low conversions its values are high, because of the large amounts of unreacted PFOSF (and, consequently, because of the small loss of weight due to reaction); in these conditions, the 'crop' yield diminishes as the temperature increases, because of the corresponding increase of the loss of weight. At high temperatures, when the conversion is higher and almost the same in every case, the 'crop' yield depends on the thermal decomposition producing larger amounts of volatile uncollected products: as the temperature increases, the amounts of these products increase and the 'crop' yield drops.

The 'crop' yield also depends on the flow rate, and this relation changes with temperature through an inversion zone (situated at about 505 °C). Below this zone, as the 'crop' yield depends on the conversion, it drops with the flow rate, and its highest values have been obtained with the highest flow rate used. Above the inversion zone the 'crop' yield increases as the flow rate diminishes, and the highest values have been obtained with the lowest flow rate. In order to explain this last behaviour, one has to suppose that at these temperatures the fluorocarbons already formed also undergo pyrolysis giving other more volatile fluorocarbons: with high flow rates, these last quickly leave the reaction zone and are not wholly collected (lower 'crop' yields); with low flow rates, they can on the contrary undergo a further thermal decomposition producing radicals which, by recombination with other radicals, can form less volatile fluorocarbons (higher 'crop' yields).

In Figure 3 the fluorocarbon yields are reported versus temperature for each flow rate, while in Figure 4 they are plotted against the flow rate at the temperatures used. The yield based upon the converted reactant always drops as the temperature increases, as it does not depend on the conversion, but only on the fluorocarbon degradation. On the contrary, the yield based upon the fed reactant depends on both factors: under conditions giving low conversions, this yield increases with the temperature because the conversion increases (see Figure 1), while when the conversion is higher the effect of the fluorocarbon degradation predominates, and the trend is similar to that previously seen. In particular, it must be pointed out that the highest yields have always been obtained with the lowest flow rate, in accordance with what was suggested for the fluorocarbon pyrolysis at high residence times. Further from Figure 4 the difference between the yield based upon the fed reactant and that one based upon the converted reactant (very large at low temperatures) becomes smaller as the temperature increases.

In Figure 5 the yields (based upon the converted reactant) for each identified fluorocarbon are shown at the various temperatures and flow rates used. The highest yields correspond to C_{10}, while the lowest ones correspond to C_{12}, which has been found only in some cases. Therefore this last fluorocarbon has been taken as a reference compound: all the compounds shown by the GLC analysis have been subdivided into two groups including the fluorocarbons with less or more carbon atoms than 12.

A comparison between the yields (based upon the converted reactant) of these two groups is shown in Figure 6. It is clear that the fluorocarbons lighter than C_{12} are prevalent at the lowest flow rate used, while those heavier than C_{12} predominate at a greater flow rate. It is thus possible to operate in experimental conditions favourable to the formation of fluorocarbons lighter or heavier than C_{12}.

CONCLUSIONS

The data obtained from the experiments carried out with PFOSF demonstrate that the pyrolysis of perfluoroalkanesulfonyl fluorides is a radical reaction producing a series of fluorocarbons. It occurs with high conversions at high temperatures and with short residence times; but high conversions can be obtained even at low temperatures when the residence time is longer. With high conversions (higher than 90 %) the fluorocarbon yield drops if the temperature, or the flow rate, increases. Further it is possible to choose the most suitable operating conditions in order to increase the yield of light or heavy fluorocarbons.

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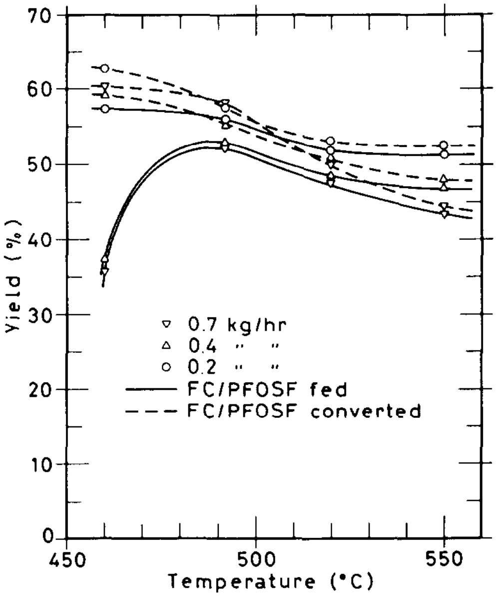

Fig. 3. Comparison between the fluorocarbon yields plotted against temperature.

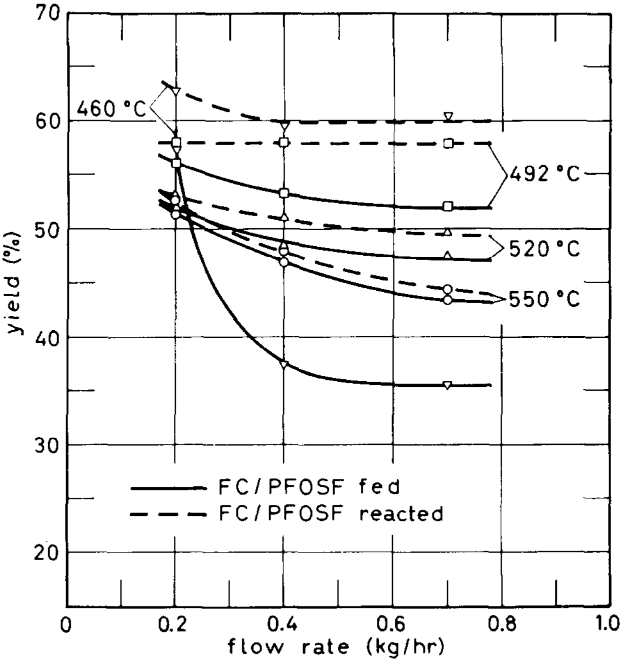

Fig. 4. Plot of the fluorocarbon yields versus flow rate.

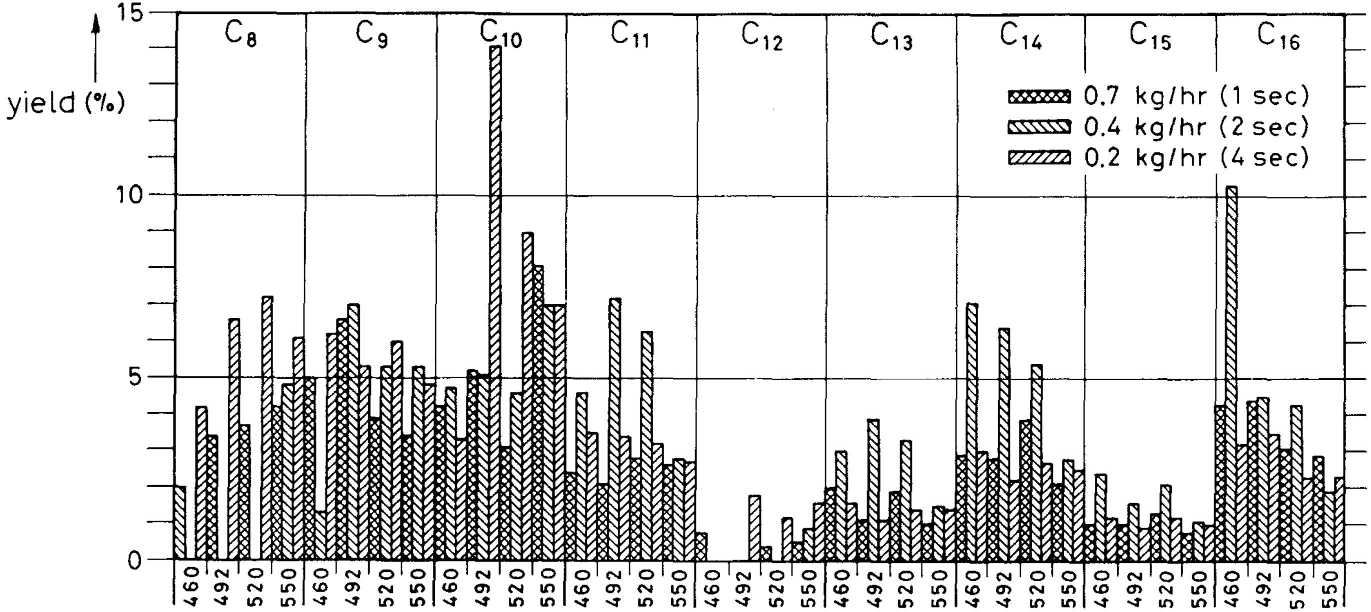

Fig. 5. Yields of the identified fluorocarbons at the various temperatures and flow rates used.

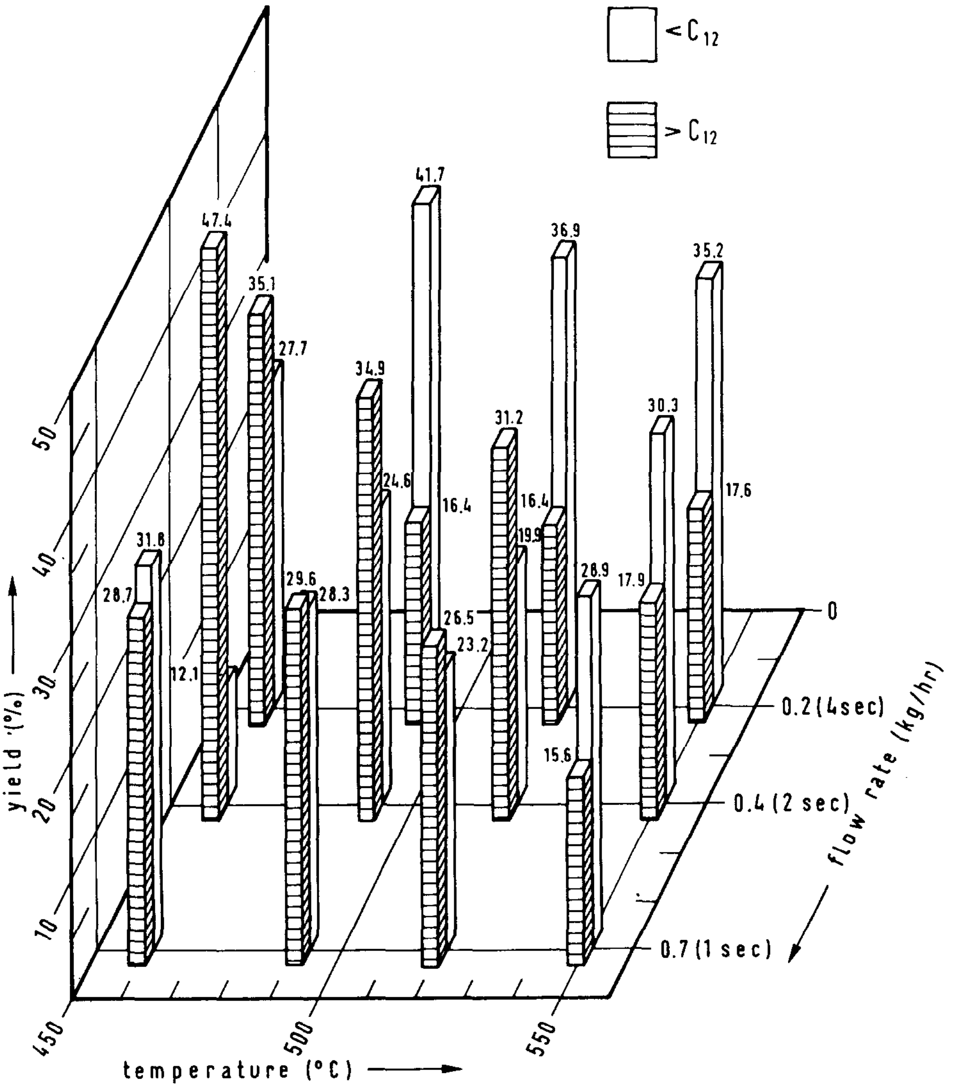

Fig. 6. Comparison between the yields of the fluorocarbon fractions lighter or heavier than C_{12}.

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