

## The Preparation of Fluorinated Cyclic Sulphides and Disulphides

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**Summary** New fluorinated cyclic sulphides and disulphides have been prepared by the vacuum pyrolysis of tetrafluoroethylene-thiocarbonyl fluoride and tetrafluoroethylene-tetrafluoroethiiran copolymers.

THE reaction between tetrafluoroethylene and elemental sulphur has been used to prepare some fluorinated cyclic sulphides and polysulphides.<sup>1</sup> The initial formation of diradical addition products of sulphur and tetrafluoroethylene, followed by intramolecular cyclisation to give sulphides and polysulphides was postulated.<sup>2</sup>

We have found that fluorinated polymers of the type  $-(CF_2)_mS(CF_2)_nS-$  decompose smoothly *in vacuo* at 500–700° to give tetrafluoroethylene, thiocarbonyl fluoride, and cyclic sulphides and disulphides. Good yields of cyclic sulphur compounds were obtained from polymers containing 10–20% of sulphur.

The copolymerisation of tetrafluoroethylene and thiocarbonyl fluoride was carried out in the gas phase using radical initiators.<sup>3</sup> Pyrolysis of these copolymers *in vacuo* at 600–700° was complete after 15 min. The products consisted of tetrafluoroethylene, thiocarbonyl fluoride, and a mixture of cyclic sulphur compounds. This mixture was separated by g.l.c. to give perfluorothietan and perfluorothian as the major components, and smaller quantities of

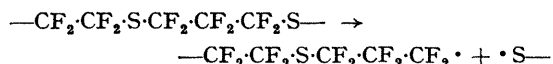
perfluorothiepan and perfluoro-1,2-dithiepan. As an example, 11.9 g. of a copolymer containing 15% of sulphur gave 4.8 g. of a mixture of tetrafluoroethylene and thiocarbonyl fluoride, 2.4 g. of perfluorothietan, 1.8 g. of perfluorothian, 0.3 g. of perfluorothiepan, and 0.1 g. of perfluoro-1,2-dithiepan.

The structures of the cyclic sulphur compounds were established by n.m.r. spectroscopy and by mass spectrometry. The <sup>19</sup>F n.m.r. spectra of the cyclic monosulphides showed peaks in the region 85–90 p.p.m. (upfield from internal CFCI<sub>3</sub>), attributed to CF<sub>2</sub> groups attached to sulphur. Other CF<sub>2</sub> groups gave peaks from 117.5 p.p.m. (in perfluorothietan) to 123.8 p.p.m. (the  $\gamma$ -CF<sub>2</sub> groups in perfluorothiepan). The CF<sub>2</sub> groups attached to sulphur in perfluoro-1,2-dithiepan gave peaks centred on 91.5 p.p.m. The other CF<sub>2</sub> groups gave peaks at 120.0 and 123.7 p.p.m.

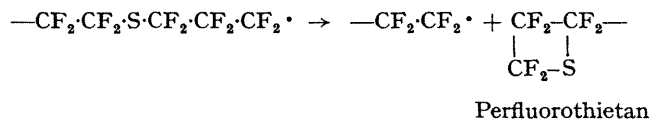
All compounds gave strong molecular ion peaks in their mass spectra. Other peaks with high intensity were *m/e* 100 (C<sub>2</sub>F<sub>4</sub><sup>+</sup>) and *m/e* 82 (CF<sub>2</sub>S<sup>+</sup>). Further intense peaks were observed as shown below.

(a) Perfluorothian and perfluorothiepan gave peaks at *m/e* 213 (C<sub>4</sub>F<sub>7</sub>S<sup>+</sup>), 163 (C<sub>3</sub>F<sub>5</sub>S<sup>+</sup>), and 131 (C<sub>3</sub>F<sub>5</sub><sup>+</sup>). (b) Perfluoro-1,2-dithiepan gave peaks at *m/e* 295 (C<sub>5</sub>F<sub>9</sub>S<sub>2</sub><sup>+</sup>), 231 (C<sub>5</sub>F<sub>9</sub><sup>+</sup>), 195 (C<sub>3</sub>F<sub>5</sub>S<sub>2</sub><sup>+</sup>), 181 (C<sub>4</sub>F<sub>7</sub><sup>+</sup>), 145 (C<sub>2</sub>F<sub>3</sub>S<sub>2</sub><sup>+</sup>), 131 (C<sub>3</sub>F<sub>5</sub><sup>+</sup>), and 64 (S<sub>2</sub><sup>+</sup>).

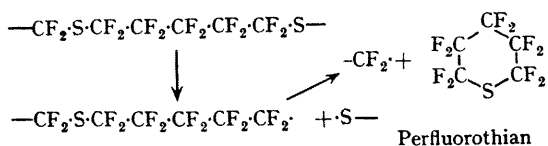
A possible mode of decomposition of these copolymers is by initial cleavage of a carbon-sulphur bond



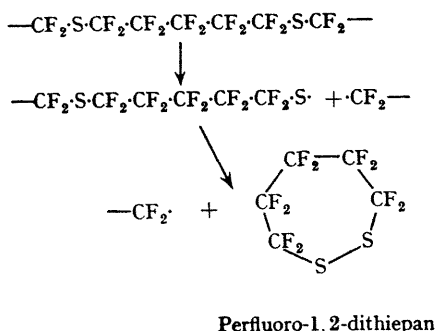
followed by cyclisation



Other cyclic sulphides would be obtained from units containing different numbers of difluoromethylene groups between sulphur atoms *e.g.*



Disulphides might be produced as follows:



The type of mechanism outlined above is consistent with

the formation of cyclic sulphur compounds which are almost exclusively those containing odd numbers of difluoromethylene groups.

Copolymers of tetrafluoroethylene and tetrafluorothian<sup>1</sup> decompose in a similar manner to give tetrafluoroethylene, thiocarbonyl fluoride, and a mixture of cyclic sulphides and disulphides. The latter mixture contained perfluorothiolan as its major constituent. Perfluorothian, perfluorothiepan, perfluoro-1,4-dithian, and perfluoro-1,2-dithian were also identified. As an example, 1.1 g. of a copolymer containing 14% of sulphur gave 0.63 g. of a mixture of tetrafluoroethylene and thiocarbonyl fluoride, 0.30 g. of perfluorothiolan, 0.04 g. of perfluoro-1,4-dithian, 0.04 g. of perfluorothian, 0.05 g. of perfluorothiepan, and 0.03 g. of perfluoro-1,2-dithian.

The structure of perfluoro-1,2-dithian was established by n.m.r. and mass spectrometry. The n.m.r. spectrum showed peaks at 111.4 p.p.m. attributed to the CF<sub>2</sub> groups attached to sulphur and peaks at 123.9 p.p.m. attributed to the other CF<sub>2</sub> groups. The mass spectrum showed a strong molecular-ion peak and other intense peaks at *m/e* 181 (C<sub>4</sub>F<sub>7</sub><sup>+</sup>), 145 (C<sub>2</sub>F<sub>3</sub>S<sub>2</sub><sup>+</sup>), 131 (C<sub>3</sub>F<sub>5</sub><sup>+</sup>), and 64 (S<sub>2</sub><sup>+</sup>). This spectrum is in contrast to that of the isomeric perfluoro-1,4-dithian which shows a strong molecular ion peak and other peaks at *m/e* = 182 (C<sub>3</sub>F<sub>6</sub>S<sup>+</sup>), 113 (C<sub>2</sub>F<sub>3</sub>S<sup>+</sup>), and 63 (CFS<sup>+</sup>).

The formation of cyclic sulphur compounds which are predominantly those containing even numbers of difluoromethylene groups supports the suggested mechanism.

Pyrolysis of polymers at 300–500° slowly gave cyclic compounds. A residue which was shown by i.r. spectroscopy, elemental analysis, and differential scanning calorimetry to closely resemble polytetrafluoroethylene was obtained on prolonged pyrolysis at these lower temperatures. This suggests that radical combination processes can take place during pyrolysis.

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<sup>1</sup> C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.* 1962, **27**, 3584; C. G. Krespan and W. R. Brasen, *ibid.*, p. 3995; W. R. Brasen, H. N. Cripps, C. G. Bottomley, M. W. Farlow, and C. G. Krespan, *ibid.*, 1965, **30**, 4188

<sup>2</sup> C. G. Krespan, "The Chemistry of Sulphides," ed. A. V. Tobolsky, Interscience, New York, 1968, p. 211.

<sup>3</sup> U.S.P. 3,240,765/1966.