

273. *Pentafluorosulphur Compounds: Preparation of Pentafluorothioacetaldehyde and (Pentafluorothio)acetic Acid.*

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Pentafluorothioacetaldehyde was prepared by acid hydrolysis of methoxyvinylsulphur pentafluoride and oxidised to (pentafluorothio)acetic acid. The dissociation constant of this acid is 3.9×10^{-3} .

THE strongly electronegative character of the pentafluorosulphur group suggested that it would be of interest to prepare pentafluorosulphur-substituted carboxylic acids from the pentafluorothioalkyl chlorides described recently,¹ and to compare their dissociation constants with those of other halogen-substituted acids. This proved unexpectedly difficult for two reasons: the instability of the pentafluorosulphur group in aliphatic compounds towards reducing agents made it impossible to use preparative methods involving organometallic reagents; and the tendency of pentafluorothioalkyl halides to eliminate hydrogen halide rather than enter into halogen-exchange reactions made it impossible to prepare alcohols or nitriles from them.

Attempts to prepare pentafluorothioalkylmagnesium halides or pentafluorothioalkyllithium compounds resulted in the formation of magnesium or lithium fluoride and a thiol

¹ Case, Ray, and Roberts, *J.*, 1961, 2066.

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or disulphide; and attempts to obtain pentafluorothioethanol from pentafluorothioethyl chloride gave only vinylsulphur pentafluoride. Efforts to prepare pentafluorothioalkyl cyanides from the chlorides met with a similar lack of success. Eventually it was discovered that methoxyvinylsulphur pentafluoride, prepared from chlorovinylsulphur pentafluoride¹ by reaction with anhydrous sodium methoxide, could be hydrolysed to pentafluorothioacetaldehyde with phosphoric acid. The aldehyde was oxidised to (pentafluorothio)acetic acid, a solid very soluble in water and volatile in steam; it was purified by sublimation under reduced pressure. The dissociation constant in aqueous solution was 3.9×10^{-3} ; it is thus intermediate in strength between monofluoroacetic acid and difluoroacetic acid.

EXPERIMENTAL

Preparation of Pentafluorothioacetaldehyde and (Pentafluorothio)acetic Acid.—2-Methoxyvinylsulphur pentafluoride. 2-Chlorovinylsulphur pentafluoride (71 g.), finely-powdered sodium methoxide (freshly prepared from 10.5 g. of sodium), and dry xylene (250 c.c.) were stirred at 0° for 96 hr. Hydrochloric acid (4N; 125 c.c.) was added, and after a short time the upper layer was separated, dried (Na₂SO₄), and fractionally distilled, giving 2-methoxyvinylsulphur pentafluoride (67 g., 82%), b. p. 115° (Found: C, 20.0; H, 3.0; F, 49.7. C₃H₅F₅OS requires C, 19.6; H, 2.7; F, 51.6%); ν_{\max} . 866vs (SF₆), 1650s and 940s (C=C), and 1240s cm.⁻¹ (C—O).

Pentafluorothioacetaldehyde. Orthophosphoric acid (220 c.c.) was heated at 110° and methoxyvinylsulphur pentafluoride (57 g.) and water (50 c.c.) were added simultaneously during 1 hr., distillation being allowed to proceed as long as the still-head temperature remained below 90°.

The distillate separated into two layers; the upper layer was combined with two ethereal extracts of the lower layer. The combined extracts were dried and distilled; after removal of the ether, pentafluorothioacetaldehyde (47 g., 89%) was collected at 79–82° (Found: C, 14.0; H, 2.0; F, 54.0. C₂H₃F₅OS requires C, 14.1; H, 1.8; F, 56.0%); ν_{\max} . 866vs and 903vs (SF₆), and at 1754s cm.⁻¹ (CHO); it gave a 2,4-dinitrophenylhydrazone, m. p. 133° (Found: C, 27.2; H, 1.7; F, 26.8; N, 15.8; S, 9.4. C₈H₇F₅N₄O₄S requires C, 27.4; H, 2.0; F, 27.1; N, 16.0; S, 9.1%).

(Pentafluorothio)acetic acid. Pentafluorothioacetaldehyde (42 g.) was stirred at 0° and a solution of sodium permanganate (14 g.) in water (150 c.c.) containing a few drops of sulphuric acid was added during 1.5 hr. Stirring was continued for a further 2 hr. at 0°, then the mixture was filtered, and decolorised by the addition of sodium metabisulphite. The clear solution was strongly acidified with concentrated sulphuric acid (ca. 10 c.c.) and extracted continuously with ether until the extract was no longer acid. Ether was removed from the extract by distillation and the semi-solid residue was purified by sublimation at reduced pressure. After two such sublimations, (pentafluorothio)acetic acid (9 g., 20%) was obtained as white crystals, m. p. 66°, subl. 45°/2 mm. (Found: C, 12.6; H, 1.7; F, 50.6%; equiv., 185.5. C₂H₃F₅O₂S requires C, 12.9; H, 1.6; F, 51.0%; equiv., 186); ν_{\max} . 850vs and 890vs cm.⁻¹ (SF₆) and 1750s and 3000s cm.⁻¹ (CO₂H). It gave a *p*-bromophenacyl ester, m. p. 82°, and an acid chloride (from thionyl chloride), b. p. 115°. The dissociation constant of the acid aqueous solution was found by potentiometric titration to be 3.9×10^{-3} .

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