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

By N. H. Ray.

Pentafluorothioacetaldehyde was prepared by acid hydrolysis of methoxyvinylsulphur pentafluoride and oxidised to (pentafluorothio)acetic acid. The dissociation constant of this acid is $3{\cdot}9 \times 10^{-3}$.

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.

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 pentafluoride [1] 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 $3{\cdot}9 \times 10^{-3}$; 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 (Na_2SO_4), and fractionally distilled, giving *2-methoxyvinylsulphur pentafluoride* (67 g., 82%), b. p. 115° (Found: C, 20·0; H, 3·0; F, 49·7. $C_3H_5F_5OS$ requires C, 19·6; H, 2·7; F, 51·6%); $\nu_{max.}$ 866vs (SF_5), 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. $C_2H_3F_5OS$ requires C, 14·1; H, 1·8; F, 56·0%); $\nu_{max.}$ 866vs and 903vs (SF_5), 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. $C_8H_7F_5N_4O_4S$ 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. $C_2H_3F_5O_2S$ requires C, 12·9; H, 1·6; F, 51·0%; equiv., 186); $\nu_{max.}$ 850vs and 890vs cm.$^{-1}$ (SF_5) and 1750s and 3000s cm.$^{-1}$ (CO_2H). 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 $3{\cdot}9 \times 10^{-3}$.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, ALKALI DIVISION RESEARCH DEPARTMENT,
WINNINGTON, NORTHWICH, CHESHIRE.
[*Received, July 17th,* 1962.]