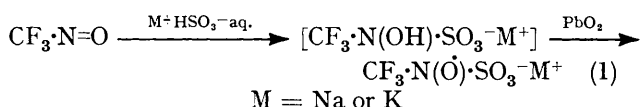


Nitroxide Chemistry. Part VI.¹ *N*-Trifluoromethylsulphamate *N*-Oxyl

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Purple solutions containing *N*-trifluoromethylsulphamate *N*-oxyl can be prepared by treatment of trifluoronitrosomethane with aqueous alkali-metal hydrogen sulphite in the presence of lead dioxide; addition of tetraphenylarsonium chloride to such a solution results in precipitation of the pale purple tetraphenylarsonium salt [CF₃·N(Ö)·SO₃⁻·Ph₄As⁺].

CURRENT interest in nitroxide chemistry prompts us to report the synthesis of the first fluorocarbon analogue of Fremy's radical, ·O·N(SO₃⁻)₂.



Deep purple, aqueous solutions of alkali-metal *N*-trifluoromethylsulphamate *N*-oxyls (1) [when M = Na, δ_F = 11.7 (s) (in p.p.m. downfield from external CF₃-CO₂H)] are easily obtained by shaking mixtures of trifluoronitrosomethane, aqueous sodium or potassium hydrogen sulphite, and lead dioxide at room temperature. Evaporation of such solutions yields unstable yellow solids (dimers?) that can be redissolved in water to give purple solutions. Addition of tetraphenylarsonium chloride to aqueous CF₃·N(Ö)·SO₃⁻K⁺ causes immediate precipitation of a purple solid which can be crystallised from

¹ Part V, R. E. Banks, D. R. Choudhury, and R. N. Haszeldine, *J.C.S. Perkin I*, 1973, 1092.

² Cf. G. R. Underwood and V. L. Vogel, *Mol. Phys.*, 1971, **19**, 621.

aqueous acetone. This has been identified as the salt CF₃·N(Ö)·SO₃⁻·Ph₄As⁺ by elemental analysis and e.s.r. spectroscopy. The splitting constants obtained were *a_F*(3) 1.04 and *a_N*(1) 1.10 mT in chloroform solution (ca. 10⁻⁴M); these values were invariant over a 100 °C temperature range, suggesting little or no deviation from planarity about the nitrogen atom,² but varied with solvent polarity in the usual way.³ The *g* value was 2.0062 ± 0.0001 and was unaffected by change in temperature and/or solvent. E.s.r. techniques have been used previously⁴ to demonstrate the formation of PhN-(Ö)·SO₃⁻ via addition of lead(IV) oxide to solutions prepared from nitrosobenzene and aqueous metal hydrogen sulphite; we confirm this, and find the *g* value to be 2.0054 ± 0.0002.

EXPERIMENTAL

E.s.r. spectra were measured with a Varian E-3 spectrometer, *g* values being determined by comparison with data

³ R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.

⁴ B. Lakatos, B. Turcsanyi, and F. Tüdös, *Acta Chim. Acad. Sci. Hung.*, 1971, **70**, 225.

from an aqueous solution of Fremy's salt (2.0056 ± 0.0001).

Sodium or Potassium N-Trifluoromethylsulphamate N-Oxyl.—Trifluoronitrosomethane (4.42 g, 44.7 mmol) was condensed, *in vacuo*, into a cold (-196°C) 300 cm³ Pyrex tube fitted with a Rotaflo needle valve and containing lead(IV) oxide (*ca.* 3 g), sodium hydrogen sulphite (1.58 g, 16.4 mmol), and water (10 cm³). The tube was allowed to warm to room temperature, then shaken for 1 h. Trifluoronitrosomethane (28.8 mmol, 64% recovery) contaminated with trifluoronitromethane (detected by i.r. spectroscopy) was removed from the tube, leaving a deep purple solution [δ_{F} (Perkin-Elmer R10 instrument operating at 56.46 MHz) -11.7 (s) (in p.p.m. from ext. $\text{CF}_3\cdot\text{CO}_2\text{H}$)] containing sodium *N*-trifluoromethylsulphamate *N*-oxyl.

Similarly, trifluoronitrosomethane (4.42 g, 44.7 mmol),

aqueous potassium hydrogen sulphite [14.1 mmol in water (10 cm³)], and lead dioxide (*ca.* 3 g) gave an intense purple solution of potassium *N*-trifluoromethylsulphamate *N*-oxyl.

Tetraphenylarsonium N-Trifluoromethylsulphamate N-Oxyl.—The purple solution containing potassium *N*-trifluoromethylsulphamate *N*-oxyl turned colourless immediately when treated with saturated aqueous tetraphenylarsonium chloride (3 cm³), and a purple precipitate (*ca.* 1 g) appeared. This was washed with water and recrystallised from aqueous acetone to give purple needles of *tetraphenylarsonium N-trifluoromethylsulphamate N-oxyl* (Found: C, 53.4; H, 3.9; N, 2.6. $\text{C}_{25}\text{H}_{20}\text{AsF}_3\text{NO}_4\text{S}$ requires C, 53.4; H, 3.6; N, 2.5%).

We are indebted to Dr. G. S. Egerton for e.s.r. facilities.

[3/2239 Received, 31st October, 1973]