

Fig. 2. Dose dependence of precipitate formation in two-phase systems saturated with oxygen. The total dose is the sum of doses absorbed in aqueous and in organic phase; the concentration of  $UO_8(NO_3)_2.2H_2O$  in aqueous phase: 1, 1 M; 2, 0.5 M; 3, 0.2 M; 4, 0.1 M; 5, 0.01 M

and/or with hydrogen peroxide. So long as the uranium peroxidic compound remains in solution it is decomposed. by the radiolytic process. As soon as its concentration exceeds the solubility limit, it is precipitated and so protected against further decomposition. The existence of the induction period may be understood in a similar way. The solubility of the uranium peroxidic compound can be affected by the nitric acid and consequently the yields  $G(\mathbf{U})$  and length of induction periods changed.

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## **New Fluorine Compounds of Technetium**

In contrast to the many fluorides, oxide fluorides and complex fluorides known for rhenium, only a few compounds of technetium have been reported, namely, the hexafluoride  $TcF_6$  (ref. 1), the trioxide fluoride<sup>2</sup>, and salts of the quadrivalent TcF=6 ion3.

Preliminary results in these laboratories indicate that the blue oxide tetrafluoride TcOF4 (m.p. 134°) and the yellow pentafluoride (m.p.  $50^{\circ}$ ) are formed as by-products in the direct fluorination of technetium metal. The oxide tetrafluoride is much like the rhenium analogue<sup>4,5</sup> in appearance and in physical properties, and the magnetic moment ( $\mu_{\text{eff}}$  (25°) = 1.76 Bohr magnetons,  $\theta = 9^{\circ}$ ) is of the expected order for a  $d_1$  compound. The pentafluoride is isostructural with chromium pentafluoride and has orthorhombic symmetry  $(a_0 = 7.6; b_0 = 5.8; c_0 = 16.6 \text{ Å}).$ It is more stable than rhenium pentafluoride<sup>4,5</sup>, but begins to decompose in glass at  $60^{\circ}$ .

Technetium hexafluoride can be reduced more easily than rhenium hexafluoride. The action of a solution of potassium iodide in iodine pentafluoride (that is, of I2 + IF<sub>4</sub>-) on the compound leads to a quadrivalent species, probably KTcF<sub>5</sub> (cf. KMnF<sub>5</sub> (refs. 8 and 9)); the corresponding reduction of ReF gives Re(V) as the salt KReF6. However, the action of solutions of alkali chlorides on TcF<sub>6</sub> in IF<sub>5</sub> gives Tc(V), and the salts NaTcF<sub>6</sub> and KTcF<sub>6</sub> have been prepared and characterized. These yellow compounds are isostructural with the corresponding ruthenium derivatives<sup>10,11</sup> and differ from the rhenium salts<sup>12</sup> (Table 1). They obey approximately the Kotani rules of magnetic behaviour<sup>13</sup> for  $d\varepsilon_2$  compounds, for example, for NaTcF<sub>6</sub>  $\mu_{eff} = 2.25$  Bohr magnetons at  $25^{\circ}$  and  $\theta = 130^{\circ}$ .

We thank the University of Birmingham for a grant for technetium, Imperial Chemical Industries, General Table 1 LATTICE CONSTANTS OF SOME COMPLEX FLUORIDES

$a_{0} = 8.18 \text{ Å}$
edral $a_{\alpha} = 5.77; \alpha = 55.8^{\circ}$
edral $a_0 = 5.80; a = 54.5^{\circ}$
$a_0 = 10.01; \ c_0 = 5.13$
edral $a_0 = 4.97; \ \alpha = 97.0^{\circ}$
edral $a_0 = 4.96; a = 97.5^\circ$

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## Formation of 2-Iminothiazolidine-4-carboxylic Acid in the Cyanobromination of Lanthionine

Sullivan and Folk<sup>1</sup> found that the symmetrical thioether, lanthionine, is converted quantitatively into cysteine by the combined action of cyanogen bromide and sodium Although we could confirm the presence of cyanide. cysteine in the reaction products we were unable to substantiate the quantitative nature of this conversion. The heterocyclic compound 2-iminothiazolidine-4-carboxylic acid, which we detected in the mixture after reaction, could have been formed by further reaction of cysteine on the cyanogen halide and could account for our low cysteine yields.

Initially, the method described by Sullivan and Folk<sup>1</sup> was followed meticulously, namely, 5 ml. of a solution of lanthionine in 0.1 N hydrochloric acid (0.1 mg/ml.) was added to 5 ml. of an aqueous NaCN solution (5 per cent). One ml. CNBr solution, prepared by adding 5 per cent NaCN to a saturated solution of bromine until the mixture was just colourless, was added. After three consecutive boilings for 30 sec and coolings for 3 min the thiol content was estimated colorimetrically using either naphthoquinone sulphonate<sup>3</sup>, phosphotungstic acid<sup>3</sup>, or brucine<sup>4</sup>. It soon became evident that the boiling period was insufficient to expel all CNBr which interferes with the estimation of thiol by any of these methods. The lanthionine/CNBr reaction mixtures were then consequently boiled continuously for 10 min. Positive tests for thiols were obtained by the nitroprusside test as well as by the methods referred to here. The quantity of thiol formed was not consistent with that expected from the amount of lanthionine used as starting material and reproducibility of results was found to be poor. A typical set of results is shown in Fig. 1.

It is known that thiazoline and thiazolidine derivatives are formed when sulphydryls are reacted on by cyanogen halides<sup>5</sup>. The presence of 2-iminothiazolidine-4-carboxylic acid in the reaction mixture was verified by descending chromatography utilizing a solvent consisting of sec. butanol, formic acid, and water (75:15:10).