

heated at 95° C. for 4 hr. in the presence of excess concentrated hydrochloric acid to dissociate the iron chelates and form the amino-acid dihydrochlorides. The solid hydrochlorides were washed several times with concentrated hydrochloric acid to remove the iron chloride, then made pH 3.5-4.0 with 1 N sodium hydroxide to form the free acid. Each fraction was filtered, washed with water until the filtrate was free of chloride, then dried under vacuum. The dry free-acid fractions were analysed spectrophotometrically by an iron increment addition method similar to that of Hill-Cottingham<sup>3</sup>. The results are given in Table 1.

Table 1

	Weight (gm.)	Purity (per cent)
EHPG from violet iron chelate	0.7130	90.0
EHPG from brown iron chelate	1.4752	98.9

Paper chromatograms of the iron chelates of these separated isomers yielded only one spot in each case. Complete visible absorption spectra of aqueous solutions of the iron chelates were identical with reported spectra<sup>1,2</sup>, except for a slight difference in the wave-length of maximum absorption. The maximum absorption of the violet chelate occurred at 485 m $\mu$  whereas that of the brown chelate occurred at 475 m $\mu$ . The reported wave-length of maximum absorption of the iron chelate of unseparated EHPG and that found in this laboratory with the starting material was 480 m $\mu$ . Attempts to determine which separated isomer was the *dl*-racemic mixture by resolution of the free acid using strychnine, brucine and amphetamine were unsuccessful.

An experiment to demonstrate any significant difference in the abilities of these isomers to translocate iron to bean plants growing in alkaline soil was conducted. To 0.246 m.moles of each isomer was added 0.224 m.moles of ferric chloride containing 20  $\mu$ c. of iron-59. The pH was adjusted to 5-7 with sodium hydroxide and the resulting solutions were diluted to 50 ml. with water. Two 20-ml. aliquots of each solution were mixed with 500 gm. of alkaline Utah soil (pH 8.4), and five bean seeds were planted in each pot. Fourteen days after planting, the bean plants were thinned out to leave two plants in each pot. Twenty-seven days after planting the primary leaves of the remaining two plants in each pot were removed, dried and ground. The uptake of iron was determined by counting a known weight of leaf sample using a well-type scintillation counter and comparing this count with that obtained from an aliquot of the original iron-59 solution. The results are given in Table 2.

Table 2

	Iron (p.p.m.)	Average
Violet iron chelate	96.0	90.5
	85.0	
Brown iron chelate	68.9	77.6
	86.2	

The small difference in average iron uptake is within expected variability among plants in an experiment of this size. Thus both forms of EHPG are effective in translocating iron to bean plants grown in alkaline soil.

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<sup>1</sup> Kroll, H., Knell, M., Powers, J., and Simonian, J., *J. Amer. Chem. Soc.*, **79**, 2024 (1957).

<sup>2</sup> Frost, A. E., Freedman, H. H., Westerback, S. J., and Martell, A. E., *J. Amer. Chem. Soc.*, **80**, 530 (1958).

<sup>3</sup> Hill-Cottingham, D. G., *Analyst*, **82**, 524 (1957).

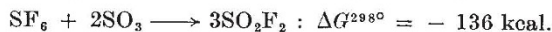
<sup>4</sup> Rubin, M., and Princiotto, J. V., *Ann. N.Y. Acad. Sci.*, **88**, 450 (1960).

## Some Chemical Reactions of Sulphur Hexafluoride

SULPHUR hexafluoride has customarily been considered to be chemically inert. It is unaffected by aqueous or fused alkali, ammonia or oxygen. The earliest report<sup>1</sup> states that sulphur hexafluoride is reductively degraded by sulphur and selenium vapours, and hydrogen sulphide at elevated temperatures, but these reactions have never been reinvestigated. The only substantiated chemical reaction of sulphur hexafluoride is that with a hot alkali metal, reaction with a film of sodium commencing at 200°<sup>2</sup>. The great stability of sulphur hexafluoride is kinetic rather than thermodynamic in origin since it is thermodynamically unstable with respect to water<sup>3</sup>. The inability of nucleophilic reagents to attack the sulphur hexafluoride molecule can be ascribed to their failure to form an S<sub>N</sub>2 type transition state because the sulphur atom has no orbital of sufficiently low energy to permit its coordination with the unshared electron pair of the entering nucleophile. Attack by a nucleophilic reagent on a fluorine atom of sulphur hexafluoride is improbable for the same reason. However, there still remains the possibility of reaction with an electrophilic reagent, for example, a strong Lewis acid, the transition state of which is formed by co-ordination of the reagent with a fluorine atom using one of its lone electron pairs. This possibility does not appear to have been investigated until now.

The reaction of sulphur hexafluoride with several 'fluorophilic' Lewis acids has now been investigated. We have found that it is reductively degraded by anhydrous aluminium chloride at moderate temperatures. Thus when the reactants were heated together in a sealed glass ampoule at 180-200° for 24 hr. a 15 per cent conversion to aluminium fluoride (identified by X-ray powder photography) occurred with the concomitant formation of chlorides of sulphur and chlorine. No compound containing sulphur and fluorine other than unchanged sulphur hexafluoride was found among the reaction products.

Using published thermodynamic data<sup>4,5</sup> it can be shown that a reaction between sulphur hexafluoride and sulphur trioxide is thermodynamically feasible:



We have found that such a reaction occurs when the reactants are heated together in a sealed glass ampoule at 250° for 24 hr. A 20 per cent conversion to sulphuryl fluoride (identified by infra-red spectroscopy) was found under these conditions; a trace of silicon tetrafluoride was the only other product. This is the first reaction of sulphur hexafluoride observed in which the hexavalent state of the sulphur is retained in the products.

No reaction was detectable between sulphur hexafluoride and boron trichloride at temperatures up to 200°.

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<sup>3</sup> Roberts, H. L., *Quart. Rev. Chem. Soc.*, **15**, 30 (1961).

<sup>4</sup> Gross, P., Hayman, C., and Levi, D. L., *Intern. Symp. Fluorine Chemistry, Birmingham* (1959).

<sup>5</sup> *National Bureau of Standards, Circ. 500.*