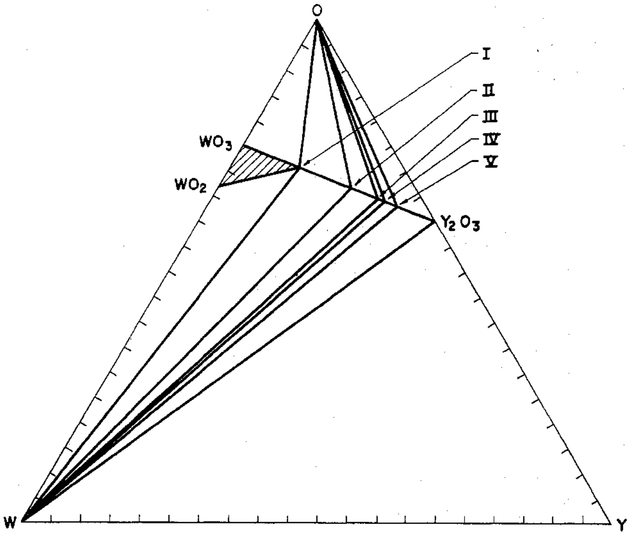

Fig. 3.—Ternary composition diagram of the system Y–W–O.

the atmosphere, it was observed that this, in fact, occurs.

It is concluded that in $Y_2O_3 \cdot WO_3$, the oxygen content is variable. The magnitude of this variation is too small to have any significance with respect to the phase diagram.

The Ternary Composition Diagram W–Y–O.—The data given above allow one to construct the ternary composition diagram of the system W–Y–O, Fig. 3. From this it is evident that no phases, other than the five reported, form from the elements tungsten, yttrium, and oxygen in the temperature range 1100–1400° at 1 atmosphere total pressure. Excluded from this conclusion are compositions in the range WO_3–WO_2–phase I, which were not investigated.

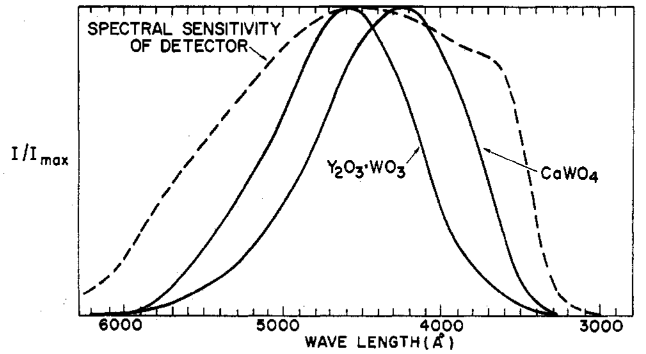

Fig. 4.—Spectral energy emission characteristics of $Y_2O_3 \cdot WO_3$ and $CaWO_4$. Mode of excitation: 2537 Å. ultraviolet light from a filtered low pressure Hg discharge. Detector: DuMont 6292 photomultiplier tube.

TABLE IV

SOME PROPERTIES OF NEW PHASES

Phase	Melting point	Color	Density, g./cc.	Weighted mean density of WO_3–Y_2O_3
I	1495 ± 5°, congruent	White	4.85	6.64
II	1700 ± 20°, incongruent	White	6.63	6.11
III	>2200°, congruent	White	6.08	5.78
IV	>2200°, congruent	White	5.95	5.70
V	>2200°, congruent, undergoes phase change	White	6.00	5.57

Properties of Tungsten–Yttrium Oxides.—Properties of the several tungsten–yttrium oxides are summarized in Table IV. It is interesting to note that whereas the normal tungstate ($Y_2O_3 \cdot 3WO_3$) has a much lower density than the weighted mean density of the constituent oxides, all the new phases have higher densities. $Y_2O_3 \cdot WO_3$ is a new photoluminescent material. It emits a bright blue-white light when excited with 2540 Å. ultraviolet light. Its emission spectrum is quite similar to that of the well known phosphor, $CaWO_4$, Fig. 4. More details on the luminescent properties of $Y_2O_3 \cdot WO_3$ will be published at a later date.

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E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

The Preparation of Difluoroamino Sulfur Pentafluoride

BY A. L. LOGOTHETIS, G. N. SAUSEN, AND R. J. SHOZDA

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Difluoroamino sulfur pentafluoride (SF_5NF_2) has been synthesized by the ultraviolet irradiation of N_2F_4 and sulfur tetrafluoride or sulfur chloride pentafluoride, or by the thermal reaction of N_2F_4 with elemental sulfur. Similarly, trifluoromethyl difluoroamino sulfur tetrafluoride ($CF_3SF_4NF_2$) has been prepared by ultraviolet irradiation of N_2F_4 and trifluoromethyl sulfur trifluoride.

In contrast to the many compounds containing sulfur, fluorine, and nitrogen, *i.e.*, $S_4N_4F_4$, SN_2F_2, $F_3S{\equiv}N$, and $N{\equiv}S{-}F$, reported by Glemser and co-workers,[1–5] where the fluorine is exclusively bonded to the sulfur, there are no examples of compounds in the literature where sulfur is bonded directly to an NF_2 group. Roberts[6] recently has suggested $SF_5NF{-}CF_3$ as the probable structure for the product of the fluorination of methyl thiocyanate with elemental fluorine, although

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(1) O. Glemser, H. Schröder, and H. Haereler, *Z. anorg. allgem. Chem.*, **279**, 28 (1955).

(2) H. Schröder and O. Glemser, *ibid.*, **298**, 78 (1959).

(3) O. Glemser and H. Schröder, *ibid.*, **284**, 97 (1956).

(4) O. Glemser and H. Haereler, *ibid.*, **287**, 54 (1956).

(5) H. Rickert and O. Glemser, *Angew. Chem.*, **72**, 585 (1960).

(6) H. L. Roberts, *Quart. Rev.* (London), **15**, 55 (1961).

the actual workers[7] proposed the alternative structure $SF_5CF_2NF_2$. This lack of representation of such an interesting class of compounds has prompted us to investigate reactions of the recently reported N_2F_4[8] with sulfur and derivatives.

Difluoroamino sulfur pentafluoride (SF_5NF_2) was prepared in small yields (6–7%) by heating equivalent amounts of N_2F_4 and elemental sulfur at 135° in a Hastelloy-lined pressure vessel, the major product of the reaction being sulfur tetrafluoride. Better yields (30–35%) of SF_5NF_2 were obtained when N_2F_4 and sulfur tetrafluoride[9] or sulfur chloride pentafluoride[10] were irradiated with a low-pressure mercury resonance lamp at room temperature in a quartz tube or, for preparative purposes, in a nickel container equipped with a calcium fluoride window.

$$[SF_4 + N_2F_4 \xrightarrow{h\nu} SF_5NF_2 + \ldots\ldots.$$

$$SF_5Cl + N_2F_4 \xrightarrow{h\nu} SF_5NF_2 + Cl_2 + \ldots\ldots$$

The formation of SF_5NF_2 from SF_5Cl and N_2F_4 is assumed to involve the SF_5 and NF_2 radicals. Johnson and Colburn[11] have presented physical evidence for the presence of NF_2 radicals, and Roberts[6,12] has shown that $SF_5\cdot$ and $Cl\cdot$ are intermediates in the reactions of SF_5Cl with olefins and oxygen. The reaction of SF_4 and N_2F_4 could go either through $SF_5\cdot$ by direct attack of a fluorine radical on SF_4 followed by combination with $\cdot NF_2$ or through $\cdot SF_4NF_2$ formed from direct attack of $\cdot NF_2$ on SF_4 followed by combination with a fluorine radical. In both cases, fluorine radicals are necessary, and they are formed during the irradiation process. The facile formation of $\cdot NF_2$ from N_2F_4 has been utilized recently to produce $ClNF_2$[13] *via* irradiation of chlorine and N_2F_4, HNF_2[14] *via* hydrogen abstraction by $\cdot NF_2$ from thiophenol, N,N-difluoroamides *via* irradiation of α-diketones[15] and N_2F_4, and N,N-difluoroamines from N_2F_4 and alkyl radicals produced from azoisobutyronitrile,[15] azoisobutane,[15] hexaphenylethane,[15] and alkyl iodides.[16]

Difluoroamino sulfur pentafluoride is a colorless gas stable to storage in a stainless steel cylinder at room temperature, and it slowly decomposes on heating. For example, after 4 hr. at 80°, only 47% SF_5NF_2 was recovered, the rest being SF_4 and NF_3. When a pure sample in a quartz tube was irradiated with a low-pressure mercury lamp, reversal of the reaction occurred to give SF_5NF_2 (48%), SF_4 (11%), and N_2F_4 (6%), with the simultaneous formation of small amounts of SF_6, NF_3, SO_2F_2, SOF_4, and N_2O. The physical properties of SF_5NF_2 are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF SF_5NF_2

Boiling point, °C.	$-17.5 \pm 0.5°$
Vapor pressure equation	$\log p = -1195/T + 7.56$
Trouton constant	21.8
Heat of vaporization	5580 cal./mole

The F^{19} n.m.r. spectrum showed a broad triplet centered at −7428 c.p.s. ($J_{N^{14}-F} \sim 120$ c.p.s.) assigned to the NF_2 group. The broad triplet structure, similar to the triplet in the F^{19} spectrum of NF_3[17] (due to the quadrupolar relaxation of the N^{14} nucleus[18]), collapses to a singlet on cooling to −75°. The SF_5 group gives two sets of multiplets with a relative intensity ratio of 1:4. Instead, however, of a simple quintuplet expected for an AX_4 type of spectrum, the single fluorine gives rise to nine distinguishable signals centered at −5534 c.p.s. The four fluorines give rise to two difficultly resolved sextets centered at −5900 and −5756 c.p.s. as is expected for an AB_4 type spectrum, with a chemical shift $\delta = 707$ c.p.s. and coupling constant $J = 144$ c.p.s. between the single apex and the four basal fluorines. It is concluded, therefore, that SF_5NF_2 exists in a tetragonal, bipyramid structure (Fig. 1) similar to the corresponding R_fSF_5 and $ROSF_5$ compounds.[19]

Trifluoromethyl difluoroaminosulfur tetrafluoride ($CF_3SF_4NF_2$) was obtained in yields of 6–8% by irradiation of CF_3SF_3 and N_2F_4 in a quartz tube with a low-pressure mercury lamp. Large amounts of SF_5NF_2, SF_4, CF_4, and SF_6 also were obtained from this reaction. Trifluoromethyl difluoroaminosulfur tetrafluoride was

$$CF_3SF_3 + N_2F_4 \xrightarrow{h\nu} CF_3SF_4NF_2 + SF_5NF_2 + SF_4 + CF_4\ldots\ldots$$

separated by gas chromatography and identified by its mass and F^{19} n.m.r. spectra. The NF_2 peak appears as a broad triplet centered at −7645 c.p.s. ($J \sim 120$ c.p.s.) because of the quadrupolar relaxation of the nitrogen, and becomes a singlet on cooling to −75°. The SF_4 group appears as an octet ($J_{F-F} = 20$ c.p.s.) in a ratio of 1:2:4:9:9:4:2:1 centered at −4822 c.p.s., the splitting being due to the two fluorines on the nitrogen and the three fluorines on the carbon, the four triplets being superimposed. The trifluoromethyl group appears as a quintet centered at 0 c.p.s. ($J_{F-F} = 22$ c.p.s.) because of the splitting from the SF_4 grouping. It appears, therefore, that $CF_3SF_4NF_2$, like SF_5NF_2, exists in a tetragonal, bipyramid structure, and that the NF_2 and CF_3 groups are situated at the two apices as shown in Fig. 2.

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(10) H. L. Roberts and N. H. Ray, *J. Chem. Soc.*, 605 (1960).

(11) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

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Experimental[20]

Difluoroamino Sulfur Pentafluoride. (a) **From Sulfur Tetrafluoride and N_2F_4.**—In a 12-l. nickel tank equipped with a calcium fluoride window were placed 25 g. (0.25 mole) of SF_4 and 26 g. (0.25 mole) of N_2F_4, and the mixture was irradiated for 80 hr. The gaseous products were condensed in a cylinder cooled at −196°. A gas chromatographic analysis of the mixture followed by mass spectrometric analysis of the individual peaks showed the presence of mainly SF_5NF_2 ($\sim$30%), N_2F_4, NF_3, SF_6, and SF_4. The mixture of gases was passed through a 5% aqueous sodium hydroxide solution using a filter stick with sintered disk of stainless steel, and SF_5NF_2 of 95% purity was collected in a trap cooled at −65°. A pure sample was obtained by preparative gas chromatography. The infrared spectrum showed very strong bands centered at 10.58, 10.95, and 11.30 μ (doublet). The mass spectrum of SF_5NF_2 is given in Table II.

TABLE II

m/e	Relative intensity, %	Ion
33	6.2	NF^+
51	6.2	SF^+
52	18.8	NF_2^+
70	11.2	SF_2^+
89	93.5	SF_3^+
108	19.5	SF_4^+
127	100.0	SF_5^+
160	0.5	SF_5NF^+

Anal. Calcd. for SF_7N: F, 74.30; mol. wt., 179. Found: F, 74.34; mol. wt., 180 (gas density).

(b) **From Sulfur Chloride Pentafluoride and N_2F_4.**—In a 12-l. nickel tank equipped with a calcium fluoride window were placed 35 g. (0.216 mole) of SF_5Cl[10] and 14.0 g. (0.135 mole) of N_2F_4, and the mixture was irradiated for 120 hr. The gaseous products were condensed in a cylinder cooled at −196° and analyzed by gas chromatography, which showed the presence of SF_5NF_2 ($\sim$34%), N_2F_4 ($\sim$15%), Cl_2 ($\sim$30%), and SF_5Cl ($\sim$8%), identified by comparison of their retention times with those of authentic samples. The SF_5NF_2 was obtained in 95% purity by scrubbing the mixture of gases with a 5% aqueous sodium hydroxide solution as above and collecting the product in a trap cooled at −65°.

(c) **From Sulfur and N_2F_4.**—Into an 80-ml. Hastelloy-C lined shaker tube containing 3.2 g. (0.1 mole) of sulfur was condensed 10.4 g. (0.1 mole) of N_2F_4, and the tube was sealed and heated at 110° for 1 hr., 120° for 1 hr., 130° for 1 hr., and 140° for 3 hr. The gaseous products were condensed in a cylinder cooled at −196° and analyzed by mass spectrometry and gas chromatography. Both analyses indicated the presence of a mixture of SF_4 (48%), N_2F_4 (30%), SOF_2 (6%), and SF_5NF_2 (6%).

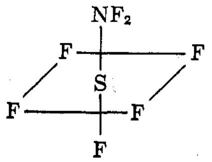

Figure 1

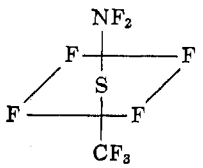

Figure 2

Difluoroamino Trifluoromethyl Sulfur Tetrafluoride ($CF_3SF_4NF_2$).—In a 3-l. flask were placed 8.2 g. (0.052 mole) of CF_3SF_3[21] and 5.0 g. (0.048 mole) of N_2F_4, and the mixture was irradiated through a quartz tube well for 7 hr. The gaseous products were condensed in a cylinder cooled at −196° and gas chromatographic analysis followed by mass spectrometric analysis of the individual peaks showed the presence of $CF_3SF_4NF_2$ ($\sim$8%), SF_6 ($\sim$40%), N_2F_4 ($\sim$9%), SF_4 ($\sim$17%), SF_5NF_2 ($\sim$4%), SO_2 ($\sim$8%), and CF_3SF_3 ($\sim$11%). The $CF_3SF_4NF_2$ was separated by preparative gas chromatography. The infrared spectrum showed strong absorption bands at 7.93, 8.6, 9.55, 10.65, 11.5, 12.5, and 14.0 μ. The mass spectrum of $CF_3SF_4NF_2$ is given in Table III.

Anal. Calcd. for CF_9NS: mol. wt., 229. Found: mol. wt., 215 (gas density).

TABLE III

m/e	Relative intensity, %	Ion
33	12.62	NF^+
44	2.19	CS^+
46	0.54	SN^+
50	2.72	CF_2^+
51	7.77	SF^+
52	8.15	NF_2^+
63	0.89	CSF^+
65	0.27	SNF^+
69	100.00	CF_3^+
70	32.26	SF_2^+
82	0.51	CF_2S^+
84	0.11	SNF_2^+
89	17.64	SF_3^+
101	0.54	CSF_3^+
103	0.16	SF_3N^+
108	0.39	SF_4S^+
120	2.82	CF_3SF^+
122	4.13	SF_4N^+
139	13.86	$CF_3SF_2^+$

Acknowledgments.—We are indebted to Mr. Miller Nelson for helpful discussions during the course of this work, and to the Physical and Analytical Division for running the gas chromatographs, infrared, n.m.r., and mass spectra.

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[20] The gas chromatographic analyses were run on a 12-ft. column containing 20% Kel-F ester (trade name for ethyl ester of perhaloöctanoic acid, Kel-F acid 8114, from Minnesota Mining and Manufacturing Co.) on firebrick at 0° with a helium flow rate of 60 ml./min. The irradiations were carried out with a low-pressure mercury resonance lamp connected to a 60 ma., 6000-volt transformer emitting mostly at 2537 Å. Nuclear magnetic resonance spectra were obtained with a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 56.4 Mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane (Freon 112). Negative frequency displacements are for resonances at lower field than the reference.

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