Methods and Numerical Results.—All reagents were prepared and handled with complete exclusion of moisture. The nitrosyl chloride was prepared by the usual reaction $NOSO_4H + HCl \rightarrow H_2SO_4 + NOCl$, and purified by means of a helix-packed column. With electrodes of bright platinum wire 1 mm. thick, having 12 mm. exposed length, and 6 mm. apart, polarization effects caused a 15% uncertainty in the evaluation of the cell constant (0.78) by reference to aqueous KCl, but the various NOCl solutions gave results consistent to 1%. These results accordingly are presented in Tables I and II for purposes of comparison.

TABLE I

CONDUCTANCES IN LIQUID NITROSYL CHLORIDE

Solute	Molarity	Temp., °C.	Spec. cond., mhos.	Molar cond.
$NOAlCl_4$	0.098	−20	1.17×10^{-2}	119
$NOFeCl_4$	.0099	−20	1.34×10^{-3}	136
$NOFeCl_4$	.0094	−21	1.26×10^{-3}	134
$NOFeCl_4$	.0094	−44	1.00×10^{-3}	106
$NOSbCl_6$	.140	−20	2.35×10^{-2}	168
$NOSbCl_6$	.140	−44	2.20×10^{-2}	157
NOCl	Pure	−20	2.88×10^{-6}	...

TABLE II

CONDUCTANCES OF $(NO)_2S_2O_7$ (SATD. IN NOCl) AT −20°

Time, hr.	0	0.75	2	15	46
Spec. cond. $\times 10^6$	4.95	25.0	48.8	23.8	14.7

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA

RECEIVED DECEMBER 11, 1947

The Effect of Sulfur Fluorides on the Viscosity of Sulfur

BY R. FANELLI

Recently, it was shown,[1,3] that the halogens, chlorine, bromine, iodine and also hydrogen sulfide and hydrogen persulfides, even when present in minute amounts, reduce the viscosity of sulfur above 160°. The degree of effectiveness decreased, with respect to the halogens, in the order shown. It was also indicated that the increasing viscosity of pure sulfur with rise in temperature might be due to polymerization of sulfur into long straight chains and that reduction of the viscosity was due to the rupture of these chains by the halogens which take up terminal positions of the segments. For example, in the case of chlorine added in the form of sulfur chloride we have

$$S_n(\text{chain}) + S_2Cl_2 \longrightarrow Cl\text{–}S\text{–}S\text{–}S \cdots S\text{–}S\text{–}SCl \text{ and/or } Cl\text{–}S\text{–}S\text{–}S \cdots S\text{–}S\text{–}S.$$

Sulfur mixtures containing 2% chlorine give viscosities under 15 centipoises throughout the entire liquid range, 115–445°. This is in sharp contrast with the maximum viscosity of pure sulfur, 93,200 centipoises, at 186–188°.

Fluorine was not tried in the earlier experiments because of the difficulty in obtaining this element. It was assumed, however, that because of its position in the halogen group it would be much more effective than chlorine. Recently, sulfur hexafluoride became available commercially and it was used in the same manner as sulfur chloride. Because of its high thermal stability, sulfur hexafluoride, if effective, would be an attractive reagent for reducing the viscosity of sulfur.

Experimental

Quantitative data were not obtained as the nature of the work was exploratory. The effect of the sulfur fluorides was determined by visual comparison of the fluidity of the treated sulfur with that of pure sulfur[2] which at 180–195° shows very little or no flow in the space of a few minutes.

Sulfur hexafluoride was bubbled for five and one-half hours through pure sulfur heated to 310° during which period little, if any, decrease in viscosity was noted. On cooling from 310 to 194° with the gas still bubbling through, the sulfur gelled indicating that the sulfur hexafluoride was comparatively ineffective in reducing the viscosity of sulfur. Apparently the stability and inertness of the hexafluoride is such that its reaction with the long sulfur chains is negligible under the conditions of the experiment.

The direct fluorination of sulfur gives in addition to the hexafluoride much smaller and variable concentrations of SF_4, S_2F_2, and (about 1%) S_2F_{10}. As revealed by Schumb,[4] these lower fluorides are removed before the purified hexafluoride is compressed into the cylinders. These lower fluorides are less stable and more reactive than the hexafluoride and might react with the long sulfur chains to appreciably reduce the viscosity.

The effect of the gases SF_4 and S_2F_2 was determined by heating in an electric furnace mixtures of pure sulfur with metallic fluorides in rotating, sealed, heavy-walled Pyrex tubes (free volume about 15 cc.). For the preparation of SF_4 the following reaction, reported to yield this compound,[4–7] was employed

$$4CoF_3 + S \longrightarrow 4CoF_2 + SF_4$$

Under the conditions of this experiment, probably some of the cobaltous fluoride was converted to sulfide. For the formation of S_2F_2 two reactions reported to yield this halide[6,7] were tried

$$2HgF + 3S \longrightarrow Hg_2S + S_2F_2$$
$$2AgF + 3S \longrightarrow Ag_2S + S_2F_2$$

---

(1) R. F. Bacon and R. Fanelli, THIS JOURNAL, **65**, 639 (1943).

(2) R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

(3) R. Fanelli, *ibid.*, **38**, 39 (1946).

(4) W. C. Schumb, *ibid.*, **39**, 421 (1947).

(5) J. Fischer and J. Werner, *Z. angew. Chem.*, **42**, 810 (1929).

(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green & Company, London, England, 1930, p. 631.

(7) Don M. Yost and Horace Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 295 and 299.

Each tube contained 7 g. of pure sulfur mixed separately with 0.3 g. and 1.0 g. of CoF_3; 0.3 g. and 1.0 g. of HgF; 0.5 g. and 1.0 g. of AgF. At the end of the experiments, all tubes were under fairly high pressure indicating formation of the gases had taken place. Only after prolonged heating (about forty-eight hours at 180–440°) was a slight reduction of the viscosity noted.

These experiments lead to the opinion that the observed failure of the sulfur fluorides to greatly affect the viscosity of sulfur is just one more instance of the abnormal behavior of fluorine and its compounds when viewed in comparison with the other halogens.

TEXAS GULF SULFUR CO., INC.
NEW YORK 17, N. Y.
RECEIVED DECEMBER 30, 1947

The Melting Point of Mustard Gas

BY W. A. FELSING, C. A. HUNTING AND S. D. FELL

Recently du Vigneaud and Stevens[1] reported a study of the preparation and purification of mustard gas (*bis*-(β-chloroethyl) sulfide) and its action on yeast. They purified the mustard by three recrystallizations from absolute ethanol and once from petroleum ether; the product had a melting point of 14.5°. The authors also cite references to other reliable melting point determinations found in relatively recent literature (*i. e.*, 14.4° and 14.5°).

In Chemical Laboratory Report No. 369, Edgewood Arsenal, Edgewood, Md., dated November 29, 1918, the authors of this note reported the purification and the melting point of mustard gas. Crude Levinstein mustard gas, melting at 8–9°, was distilled at 10 mm. pressure, yielding a distillate melting at 13.6°. This material was thrice distilled at pressures below 10 mm. and subjected to partial freezing. It was collected on a Buchner filter and the adhering liquid was removed rapidly by suction. The collected crystals were melted and again the resulting liquid was partially re-frozen and the crystals collected as before. In all, the crystals were partially frozen, drained and remelted seven times. The final product weighed about 750 g. (original volume of distilled mustard gas was about 1 gallon).

The melting point of the purified mustard gas was determined by the usual procedure of taking temperature readings every thirty seconds until every trace of the crystals had disappeared. The melting point was determined graphically from a time–temperature plot. The melting point apparatus and the thermometer were kindly loaned by the Physical Chemistry Division of Johns Hopkins University. The short-range thermometer, whose ice-point was carefully checked and which was calibrated by the Physikalische Technische Reichsanstalt (P.R.T. No. 26260) was calibrated in 0.1° and temperatures could be estimated to 0.02° by the aid of a magnifier. Two series of determinations yielded a melting point of 14.45° and one of 14.44°.

Both of these values agree markedly well with the values given and cited by du Vigneaud and Stevens.

This note was suggested as a historical record by Chemical Corps Technical Command, Army Chemical Center, Md.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS
RECEIVED JANUARY 9, 1948

---

[1] du Vigneaud and Stevens, THIS JOURNAL, **69**, 1808 (1947).

The Preparation of *p*-Dimethylaminobenzoic Anhydride

BY WILLIAM S. FONES

In connection with other work under way in this Laboratory it was necessary to prepare *p*-dimethylaminobenzoic anhydride. By heating *p*-dimethylaminobenzoic acid in acetic anhydride V. Meyer and Askenasy[1] isolated a substance (m. p. 109°) that analyzed correctly for an addition complex consisting of one molecule of *p*-dimethylaminobenzoic anhydride and one of acetic anhydride. This work was repeated by Van Der Haar,[2] who reported the complex (m. p. 109°) lost acetic anhydride when heated above its melting point to yield a substance sintering at less than 200° and melting at 218°. He assumed the latter material to be the free anhydride.

This assumption is shown to be in error by the present work. The anhydride was prepared by the action of phosphorus pentoxide on *p*-dimethylaminobenzoic acid in boiling xylene (method A) or by adding phosphorus oxychloride to a solution of *p*-dimethylaminobenzoic acid and triethylamine in chloroform (method B). The product from either reaction upon recrystallization from benzene had a m. p. of 157–159° (cor.); a mixed melting point determination showed no depression. By method A the anhydride was obtained in a yield of 30% based on acid used with a 36% recovery of unreacted acid whereas a 50% yield was obtained by method B but no starting material was recovered.

The pure compound gave the expected analysis and was further characterized by conversion to the known methyl *p*-dimethylaminobenzoate,[3] and *p*-dimethylaminobenzamide[4] through the action of methanol and ammonia, respectively.

Experimental

***p*-Dimethylaminobenzoic Anhydride (Method A).**—To a stirred suspension of 9.1 g. of *p*-dimethylaminobenzoic acid in 450 ml. of refluxing *m*-xylene there was added 8 g. of phosphoric anhydride. Stirring and refluxing were continued for seven hours with an additional 8-g. portion of phosphoric anhydride being added at the end of the first,

---

[1] V. Meyer and P. Askenasy, *Ber.*, **26**, 1365 (1893).

[2] A. W. Van Der Haar, *Rec. trav. chim.*, **47**, 324 (1928).

[3] John Johnston, *Proc. Roy. Soc.* (*London*), **A78**, 82 (1906).

[4] German Patent 77,329 (1892); *Frdl.*, **4**, 173 (1899).