

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

Some Reactions of Bis-(pentafluorosulfur) Peroxide

BY CLAUDE I. MERRILL AND GEORGE H. CADY

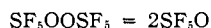
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Reactions between bis-(pentafluorosulfur) peroxide and NO, CF₂Cl₂, C₂F₄, CF₃OOCF₃, S₂O₆F₂, SO₂ and SF₄ have been observed. It has been found that bis-(pentafluorosulfur) peroxide acts to introduce sulfur oxide pentafluoride groups into molecules by substitution and oxidative addition. Side reactions often occur. These side reactions include the decomposition of the peroxide into simpler products and also include oxygenation and, occasionally, fluorination. The new substances, SF₅OOCF₃, SF₅OOSO₂F, (SF₅)₂SO₄ and *cis*-(SF₅O)₂SF₄, have been characterized. A new method for the synthesis of SF₅OSO₂F has been found and properties of the compound have been determined.

Peroxydisulfuryl difluoride reacts with a number of substances to give fluorosulfonates¹⁻⁵ and also acts as an oxygenating agent in some instances.⁴ The purpose of the present study was to investigate some reactions of the related substance, bis-(pentafluorosulfur) peroxide (SF₅OOSF₅), to learn whether its chemical behavior is analogous to that of peroxydisulfuryl difluoride. Certain parallels between the reactions of the two substances were observed, but in nearly all cases yields of predicted products were lower than expected.

The chemical reactivity of bis-(pentafluorosulfur) peroxide seems to be low unless it is subjected to conditions that decompose the peroxide. Its reactivity is much less than that of peroxydisulfuryl difluoride. The decomposition may be achieved thermally or by ultraviolet irradiation. Thus, reaction begins to occur between the sulfur dioxide and bis-(pentafluorosulfur) peroxide close to the same temperature where the thermal decomposition of the peroxide⁶ becomes first noticeable. Also, reaction between bis-(pentafluorosulfur) peroxide and a number of substances (*e.g.*, F₂, CF₂Cl₂, C₂F₄, NO, CF₃OOCF₃, S₂O₆F₂, SO₂ and SF₄) does not take place at room temperatures unless ultraviolet light is provided.

From the above observations it seems likely that the active species in these reactions is not molecular bis-(pentafluorosulfur) peroxide but sulfur oxide pentafluoride free radicals that are formed by oxygen-oxygen bond cleavage in the peroxide, as



These free radicals may then react. Thus, bis-(pentafluorosulfur) peroxide in the presence of ultraviolet light displaces chlorine from CF₂Cl₂, adds two sulfur oxide pentafluoride groups to SF₄ and generates a non-symmetrical peroxide (*e.g.*, CF₃OOSF₅) when mixed with another peroxide (*e.g.*, CF₃OOCF₃).

The reactions of bis-(pentafluorosulfur) peroxide to give compounds containing the SF₅O group are in general much farther from quantitative than reactions of S₂O₆F₂ which give compounds containing the SO₃F group. Yields of predicted products are usually decreased to a small extent by the decomposition of the SF₅OOSF₅ to sulfur hexafluoride, thionyl tetrafluoride and oxygen. However, side reactions of oxygenation or fluorination or both often occur (*e.g.*, with CF₂Cl₂, C₂F₄, SO₂, SF₄ and NO). In some instances these side reactions are so extensive that none of the desired product is detected (*e.g.*, with CF₂Cl₂, C₂F₄ and NO).

Where oxygenation occurs, *e.g.*, reactions with C₂F₄, CF₂Cl₂ and SF₂, bis-(pentafluorosulfur) oxide appears as a product. This substance may originate as the result of reduction of an SF₅O· radical to SF₅· followed by combination of the SF₅· radical with SF₅O·. Col-

lisional deactivation of an intermediate species, such as SF₅OSF₄·, could possibly increase the lifetime of that species long enough to allow the addition of a second sulfur oxide pentafluoride radical forming a stable molecular species. This would seem to be the case where *cis*-bis-(pentafluorosulfoxy)-sulfur tetrafluoride (SF₄(OSF₅)₂) is formed in greatly enhanced yields in a liquid phase reaction compared to a gas phase reaction.

It is striking that the reaction between sulfur tetrafluoride and bis-(pentafluorosulfur) peroxide produces only the *cis* configurations of bis-(pentafluorosulfoxy) sulfur tetrafluoride. There is no apparent reason why the *cis* isomer should be more stable than the *trans* form. Actually, steric considerations would predict the *trans* isomer to be the most stable configuration. The reason that only the *cis* isomer is formed probably stems from the non-symmetrical structure of sulfur tetrafluoride. Further study is indicated for the elucidation of this reaction.

Experimental

Materials.—Nitric oxide, sulfur dioxide, carbon monoxide, fluorine, nitrogen and difluorodichloromethane were obtained in gas cylinders from commercial suppliers. A gas cylinder of sulfur tetrafluoride was donated to this Laboratory by E. I. du Pont de Nemours and Co., Inc. Iodine and sulfur trioxide were reagent grade materials. Tetrafluoroethylene was produced by pyrolysis of Teflon in an iron vessel at 550°, and peroxydisulfuryl difluoride was prepared by the method described by Shreeve.⁴ Bis-(trifluoromethyl) peroxide⁵ was prepared by irradiation of trifluoromethyl hypofluorite with a mercury-arc lamp, according to the equation $2\text{CF}_3\text{OF} \xrightarrow{h\nu} \text{CF}_3\text{OOCF}_3 + \text{F}_2$. A high pressure reaction between pentafluorosulfur hypofluorite and thionyl fluoride was used to synthesize bis-(pentafluorosulfur) peroxide.⁶ Purification of the products was achieved by fractional codistillation.⁷ A Swarts' reaction was used to produce thionyl fluoride,⁸ and pentafluorosulfur hypofluorite was formed by the catalytic fluorination of thionyl fluoride.⁹

General Methods.—Infrared spectra were obtained using a Perkin-Elmer model 21 infrared spectrometer equipped with sodium chloride optics. A 10-cm. cell with silver chloride windows contained the gaseous samples.

Nuclear magnetic resonance spectra were obtained using a Varian model 4311 B high resolution spectrometer.

Mass Spectra were recorded by a Consolidated model 21-103 mass spectrometer.

Molecular weights were measured using a calibrated gas density flask which could be filled at room temperature to a known pressure up to one atmosphere while attached to a vacuum line for handling gases.

Liquid densities were obtained using single capillary pycnometers.

Vapor pressures were determined as a series of boiling points at different pressures by the method previously described.¹⁰

Elemental analyses were obtained for SF₅OOCF₃, SF₅OOSO₂F, SF₅OSO₂F, (SF₅)₂SO₄ and *cis*-(SF₅O)₂SF₄ following a potassium fusion at 500° for 6 hours. Sulfide, formed by the alkali metal fusion, was determined by titration with standard iodine solution. Fluorine was determined by the potentiometric null point titration method of O'Donnell and Stewart.¹¹

(1) J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **81**, 4166 (1959).

(2) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 352 (1960).

(3) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 353 (1960).

(4) J. M. Shreeve and G. H. Cady, *ibid.*, **83**, 4521 (1961).

(5) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

(6) C. I. Merrill and G. H. Cady, *ibid.*, **83**, 298 (1961).

(7) G. H. Cady and D. P. Siegarth, *Anal. Chem.*, **31**, 618 (1959).

(8) H. S. Booth and F. C. Mericola, *J. Am. Chem. Soc.*, **62**, 640 (1940).

(9) F. B. Dudley, G. H. Cady and D. F. Eggers, *ibid.*, **78**, 1553 (1956).

(10) W. P. Van Meter, Ph.D. Thesis, University of Washington, 1959.

(11) T. A. O'Donnell and D. F. Stewart, *Anal. Chem.*, **33**, 337 (1961).

TABLE I
 PHYSICAL PROPERTIES OF NEW COMPOUNDS

	SF ₅ OOCF ₃	SF ₅ OOSF ₂ F	SF ₅ OSO ₂ F	(SF ₅) ₂ SO ₄	(SF ₅ O) ₂ SF ₄
Mol. wt., exptl.	228 ± 0.5	242 ± 1	226 ± 0.4	350 ± 2	394 ± 1
Calcd.	228.1	242.1	226.1	350.2	394.2
Den., g./ml. at 20°	1.760	1.841	1.867	2.041	2.110
Vol. coeff. at 20° × 10 ³	2.26	1.67	1.70	1.35	1.44
M.p., °C.	-136	...	Ref. 14	-48	-82
B.p., °C.	7.7	54.1	39.6	101.9	94.0
Δ <i>H</i> _{vap} , ^a kcal./mole	6.40	7.17	Ref. 14	8.80	8.52
Trouton constant	22.8	21.9	22.1	23.5	23.2
N.m.r. parameters at 40 megacycles ^b					
SF ₅ group	Ref. 12		Ref. 12, 13	Ref. 12	
δ basal F, c.p.s.		0			0
δ apex F, c.p.s.		84.7			407
<i>J</i> (basal to apex), c.p.s.		155			153
SO ₂ F group δ, c.p.s.		751			...
<i>J</i> (basal to SO ₂ F), c.p.s.		2.9			
SF ₄ group					
δ A pair, c.p.s.		...			-184.0
δ B pair, c.p.s.		...			-446.5
<i>J</i> (A to B), c.p.s.		...			153
Quantitative data					
S, exptl., %	14.4	26.2	27.6	27.4	24.0
Calcd., %	14.1	26.5	28.3	27.4	24.4
F, exptl., %	66.4	46.6	48.9	53.8	67.0
Calcd., %	66.6	47.1	50.4	54.3	67.5
Oxid. eq.	1.98	1.997
Calcd.	2.00	2.00			

^a Δ*H*_{vap} was obtained by use of the Clausius-Clapeyron equation. ^b Positive values of chemical shift (δ) are located upfield from the basal fluorine resonances of the SF₅ group.

Ultraviolet irradiation involved the use of a 350 watt Hanau mercury vapor lamp which was placed in a quartz glass finger extending diametrically through a Pyrex glass reaction flask. The lamp was cooled by water flowing within the finger and around the lamp.

Behavior toward Iodine.—Iodine reacts readily with peroxydisulfuryl difluoride at room temperature to give I(SO₂F)₂.²

A small quantity of iodine was placed in a 250-ml. Pyrex glass bulb and 100 mm. pressure of bis-(pentafluorosulfur) peroxide was admitted. Since no reaction occurred, the bulb was first gently heated with a gas flame followed by a stronger application of heat. Since there was no indication of the formation of an iodine compound, no further effort was spent on this reaction.

Behavior toward Nitric Oxide.—Nitric oxide and peroxydisulfuryl difluoride react at room temperature to give NOSO₂F.³

Fifty mm. pressure of bis-(pentafluorosulfur) peroxide and 100 mm. of nitric oxide were placed in a 250-ml. quartz glass bulb. No reaction was observed. Irradiation of the flask for 4 hours by a mercury arc lamp resulted in extensive etching of the bulb and the formation of reddish-brown nitrogen dioxide. No solid product analogous to the nitrosyl fluorosulfonate was formed.

Reaction with Difluorodichloromethane.—Many chlorides, including carbon tetrachloride, are oxidized by peroxydisulfuryl difluoride at room temperature, and chlorine is one of the products. In general bis-(pentafluorosulfur) peroxide has not been found to liberate chlorine from chlorides at room temperature; however, irradiation by ultraviolet light did produce chlorine in the case now to be described.

Sixty mm. pressure each of bis-(pentafluorosulfur) peroxide and difluorodichloromethane were placed in a 5-liter vessel and irradiated by a mercury arc lamp for 12 hours. A green color appeared in the gas mixture indicating that chlorine had been evolved. Products identified by their infrared spectra after separation by fractional codistillation⁷ were silicon tetrafluoride, sulfur hexafluoride, carbonyl fluoride, carbon dioxide, sulfuryl fluoride, thionyl tetrafluoride, difluorodichloromethane, bis-(pentafluorosulfur) oxide and bis-(pentafluorosulfur) peroxide. Silicon tetrafluoride, carbonyl fluoride, carbon dioxide, bis-(pentafluorosulfur) oxide and chlorine were the main products. The carbon dioxide, sulfuryl fluoride and silicon tetrafluoride probably arose due to the action of carbonyl fluoride and thionyl tetrafluoride on the Pyrex glass reaction vessel, and the sulfur hexafluoride and thionyl tetrafluoride were most likely produced by the decomposition of bis-(pentafluorosulfur) peroxide. Apparently the main reaction was: SF₅OOSF₅ + CF₂Cl₂ $\xrightarrow{h\nu}$ COF₂ + SF₅OSF₅ + Cl₂.

Reaction with Tetrafluoroethylene.—Peroxydisulfuryl difluoride readily adds across the double bond in tetrafluoroethylene to

give C₂F₄(SO₂F)₂. A similar reaction between SF₅OOSF₅ and tetrafluoroethylene (at pressures of 210 and 70 mm., respectively) did not occur. When the mixture was irradiated for 48 hours by a mercury vapor lamp a liquid collected in the vessel. Because of its low volatility the liquid was not studied further. It must have been a polymer. The gases remaining in the reaction flask were found to contain SiF₄, SF₆, SO₂F₂, COF₂, SOF₄,

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 CF₃CF, (SF₅)₂O, SF₅OOSF₅ and at least three other materials which were not identified. If the addition product was present, it was there only in very small amount.

Reaction with Bis-(trifluoromethyl) Peroxide.—Equal quantities of bis-(trifluoromethyl) peroxide and bis-(pentafluorosulfur) peroxide were placed in a 3-liter glass vessel. After mercury-arc irradiation for 7 days, a mixture containing about equal amounts of bis-(trifluoromethyl) peroxide, pentafluorosulfur trifluoromethyl peroxide and bis-(pentafluorosulfur) peroxide was obtained. Small quantities of more volatile substances were also detected during fractional codistillation⁷ of the products. The reaction can be represented by the equation: SF₅OOSF₅ + CF₃OOCF₃ $\xrightarrow{h\nu}$ 2SF₅OOCF₃. Pentafluorosulfur trifluoromethyl peroxide was also produced, but in low yield, by combining SF₅OF with COF₂ at 210°: SF₅OF + COF₂ = SF₅OOCF₃. The physical properties of pentafluorosulfur trifluoromethyl peroxide are presented in Tables I-III.

Reactions of SF₅OOSF₅ with Peroxydisulfuryl Difluoride.—Equal amounts of peroxydisulfuryl difluoride and bis-(pentafluorosulfur) peroxide at a total pressure of 200 mm. were irradiated by a mercury arc lamp for 4 days. Separation of the products by fractional codistillation showed approximately equal quantities of bis-(pentafluorosulfur) peroxide, pentafluorosulfur fluorosulfuryl peroxide and peroxydisulfuryl difluoride along with very small amounts of more volatile substances. An equation describing the reaction is: SF₅OOSF₅ + S₂O₆F₂ $\xrightarrow{h\nu}$ 2SF₅OOSO₂F.

The same new compound has been produced in low yield by the reaction of pentafluorosulfur hypofluorite with sulfur trioxide at about 210°. Many by-products were obtained.

Since pentafluorosulfur fluorosulfuryl peroxide could not be completely separated from peroxydisulfuryl difluoride by frac-

(12) C. I. Merrill, S. M. Williamson, G. H. Cady and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

(13) R. K. Harris and K. J. Packer, *J. Chem. Soc.*, 4736 (1961). The synthesis of SF₅OSO₂F was mentioned in this article, but no physical constants were published.

(14) H. J. Emelús and K. J. Packer, *ibid.*, 771 (1962).

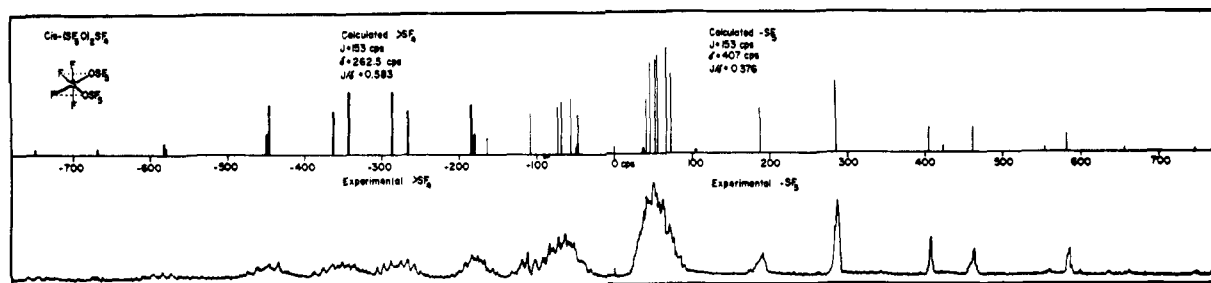


Fig. 1.—Nuclear magnetic resonance spectrum of *cis*-(SF₅O)₂SF₄ obtained at 40 Mc. The zero on the scale was taken as the center of the basal fluorine atom resonances of the -SF₅ group. The apex fluorine atom resonances of the -SF₅ group are located 407 c.p.s. upfield from this point. The A and B resonances of the >SF₄ portion of the spectrum are shifted -184.0 c.p.s. (downfield) and -446.5 c.p.s. from the zero point.

tional codistillation⁷ or purified by gas chromatography, because of reaction with the column packing, a semi-purified sample was first contacted with iodine. This reacted with all of the peroxydisulfuryl difluoride within a 30-minute period. The pentafluorosulfur fluorosulfonyl peroxide was then isolated in high purity from the remaining products by fractional codistillation.

Values for a number of physical properties of pentafluorosulfur fluorosulfonyl peroxide are listed in Tables I-III.

Reaction of SF₅OOSF₅ with Sulfur Dioxide.—A mixture of sulfur dioxide (70.5 mm.) and bis-(pentafluorosulfur) peroxide (60.7 mm.) was slowly warmed up from room temperature in a nickel vessel of 1.46-liter volume. Below 170° the mixture followed the gas laws (suggesting no reaction). Above 170°

This pressure increase was probably due to thermal decomposition of the peroxide. Separation of the reaction products, by fractional codistillation, with identifications being made by infrared spectra, gave the substances: silicon tetrafluoride, sulfur hexafluoride, sulfur fluoride, thionyl tetrafluoride and bis-(pentafluorosulfur) oxide. The bis-(pentafluorosulfur) oxide was also identified by its molecular weight (exptl. 270.3, theor. 270.1). Thionyl tetrafluoride and bis-(pentafluorosulfur) oxide were the principal products. Thus, ignoring peroxide decomposition, the reaction may be expressed as SF₅OOSF₅ + SF₄ → SOF₄ + SF₅OSF₅.

TABLE II

VAPOR PRESSURES

SF ₅ OOCF ₃ : log P _{mm} = 7.11733 - 1020.00/T - 47,780.2/T ²							
P _{mm} , exptl.	16.0	71.0	131.2	298.6	469.4	689.5	759.9
P _{mm} , calcd.	16.0	70.6	131.7	298.6	470.7	690.0	759.7
T, °K.	210.8	232.6	243.3	259.4	269.4	278.5	280.9
SF ₅ OOSO ₂ F: log P _{mm} = 5.58822 - 281.402/T - 198,002/T ²							
P _{mm} , exptl.	4.0	12.3	34.8	185.1	482.1	628.5	783.4
P _{mm} , calcd.	3.6	12.3	35.7	185.0	484.6	625.0	783.4
T, °K.	228.2	243.4	259.1	290.2	314.1	321.4	328.3
SF ₅ OSO ₂ F: log P _{mm} = 6.48848 - 768.928/T - 112,506/T ²							
P _{mm} , exptl.	5.1	17.4	76.0	224.5	325.5	523.7	756.0
P _{mm} , calcd.	4.8	17.4	75.7	222.3	323.8	523.3	756.4
T, °K.	220.4	237.0	260.5	282.0	290.6	302.6	312.7
(SF ₅) ₂ SO ₄ : log P _{mm} = 6.96637 - 1169.73/T - 135,496/T ²							
P _{mm} , exptl.	42.7	227.2	298.5	425.4	564.1	644.0	793.0
P _{mm} , calcd.	42.7	227.7	298.5	424.8	564.6	643.0	793.7
T, °K.	303.0	340.2	347.3	357.1	365.5	369.5	376.2
<i>cis</i> -(SF ₅ O) ₂ SF ₄ : log P _{mm} = 7.20850 - 1333.13/T - 94,039.5/T ²							
P _{mm} , exptl.	82.3	199.2	295.7	381.4	563.6	687.1	747.8
P _{mm} , calcd.	82.3	198.7	295.8	382.4	563.6	688.2	747.6
T, °K.	309.3	329.6	339.8	346.8	358.0	364.1	366.7

pressures progressively less than those predicted by the ideal gas laws were observed (suggesting a reaction to give a smaller number of molecules). The reactor was held at 225° for 5 hours and the products were then removed and separated by fractional codistillation. The identified products were SiF₄, SF₆, SO₂F₂, SOF₄, SF₅OSF₅ and two new substances, SF₅OSO₂F and (SF₅)₂SO₄. A liquid product of low volatility which condensed in the vacuum line as products were withdrawn from the hot reactor was not identified. After this work was done the compound SF₅OSO₂F (pentafluorosulfur fluorosulfonate) was reported in the literature by Harris and Packer,¹³ but its properties were not given. During the handling of the products the two new substances were first obtained as a mixture by fractional codistillation. The two substances were then separated by gas chromatography.

Reaction was again observed between sulfur dioxide and bis-(pentafluorosulfur) peroxide when a mixture of equimolar quantities of the two substances in a 250-ml. quartz glass bulb was irradiated for 4 days by an external mercury arc lamp. The main product was an oil of low volatility. No bis-(pentafluorosulfur) sulfate was detected and the yield of pentafluorosulfur fluorosulfonate was much smaller than in the high temperature reaction.

Physical properties for pentafluorosulfur fluorosulfonate and bis-(pentafluorosulfur) sulfate are given in Tables I-III.

Reaction of SF₅OOSF₅ with Sulfur Tetrafluoride.—A mixture of sulfur tetrafluoride (247.9 mm.) and bis-(pentafluorosulfur) peroxide (220.8 mm.) was subjected to gradually increasing temperature in a 1.46-liter nickel vessel. At about 210° an increase in pressure above that expected by the ideal gas law was noted, indicating that molecular addition was not occurring.

TABLE III
INFRARED SPECTRA

—SF ₅ OOCF ₃ —		—SF ₅ OOSO ₂ F—	
ν, cm. ⁻¹	Assignment	ν, cm. ⁻¹	Assignment
1493m		1494s	S=O str.
1291vs	C—F str. ¹⁵	1247s	S=O str.
1248vs	C—F str.	936vs	S—F str.
1207vs	C—F str.	910s	S—F str.
963s	S—F str. ¹⁶	883s	S—F str.
931vs	S—F str.	848vs	S—F str.
880vs	S—F str.	796ms	
748m	S—F str.	740m	S—F str.
SF ₅ OSO ₂ F (ref. 14)		<i>cis</i> -(SF ₅ O) ₂ SF ₄	
(SF ₅) ₂ SO ₄			
1478s	S=O str.	970vs	S—F str.
1240s	S=O str.	953vs	S—F str.
948vs	S—F str.	937vs	S—F str.
899s		903m	
877s		850vs	S—F str.
833vs	S—F str.	806vs	
727m	S—F str.	786vs	
		705m	S—F str.

In another reaction between sulfur tetrafluoride and bis-(pentafluorosulfur) peroxide 200 mm. pressure of an equimolar mixture of the two substances was irradiated by a mercury arc lamp for 12 hours in a 3-liter flask. During fractional codistillation of the products *cis*-bis-(pentafluorosulfoxy) sulfur tetrafluoride (*cis*-(SF₅O)₂SF₄) was observed in very small yield (estimated to be less than 1% yield). Again as previously noted thionyl tetrafluoride and bis-(pentafluorosulfur) oxide were the main products. The formation of the bis-(pentafluorosulfoxy) sulfur tetrafluoride may be represented by the equation SF₅OOSF₅ + SF₄ = (SF₅O)₂SF₄.

Later an equimolar mixture of sulfur tetrafluoride and bis-(pentafluorosulfur) peroxide was sealed into a quartz glass tube (10 cm. long, 8 mm. o.d.) so that about three-fourths of the tube was filled with liquid. For a 4-day period at room temperature the tube was irradiated by an external mercury arc lamp. Separation by fractional codistillation gave (SF₅O)₂SF₄ in about 70% yield.

In Tables I-III values for physical constants of *cis*-bis-(pentafluorosulfoxy) sulfur tetrafluoride are listed. The n.m.r. spectrum provides strong evidence for the *cis* structure. After preliminary measurements on the experimental spectrum, two theoretical spectra were computed with the aid of an IBM

(15) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., Vol. II, 1950, p. 456.

(16) L. H. Cross, G. Cushing and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961).

program.¹⁷ One spectrum was computed as a pure $>SF_4$ spectrum (A_2B_2 system), and the other was calculated as a pure $-SF_3$ spectrum (AB_3 system). By joining these two calculated spectra together, a theoretical spectrum for the *cis* form of bis(pentafluorosulfoxy) sulfur tetrafluoride was constructed that ignored interactions between the fluorine atoms of the different groups. In Fig. 1 it may be seen that good correlation between the centers of extensively split bands of the experimental spectrum and computed lines of the theoretical spectrum was ob-

(17) Program furnished by Professor K. B. Wiberg, University of Washington.

tained. All bands in the spectrum are explained by this treatment. The *trans* form must be either totally absent in this preparation or present in quite small quantity, because the $-SF_4$ part of its spectrum would be expected to give an easily observable single band.

Acknowledgments.—The authors thank Professor Kenneth B. Wiberg for providing a computer program and E. I. du Pont de Nemours and Company for the sample of sulfur tetrafluoride. Mass and n.m.r. spectra were obtained with the aid of B. J. Nist.

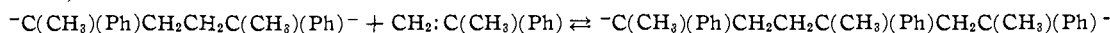
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, N. Y.]

Kinetics and Equilibrium of the System Living α -Methylstyrene Dimer + Monomer \rightleftharpoons The Living Trimer. Application of a Stirred-flow Reactor for Studies of Reversible Addition Reactions

BY C. L. LEE, J. SMID AND M. SZWARC

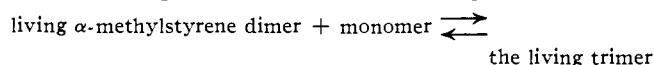
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The kinetic studies of a reversible reaction $A + B \rightleftharpoons C$ in a stirred-flow reactor makes it possible to determine simultaneously the rate constants of the forward and backward reactions by plotting $\{[A]_0/([B]_0 - [B]_t) - 1\} [B]_t$ vs. $1/t$, where t denotes the residence time. Such a plot produces a straight line with a slope equal to the rate constant of the forward reaction and an intercept giving the equilibrium constant of the process. This technique has been applied to studies of the polymerization of the living α -methylstyrene dimer to the living trimer, *i.e.*

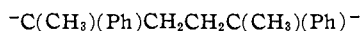


At 25° the rate constant of propagation was found to be 7 times greater than that for a high-molecular weight living poly- α -methylstyrene, whereas the corresponding rate constant of depropagation was lower by about a factor of 100. The equilibrium constant was found to be in fair agreement with the value derived from the equilibrium studies by Vrancken, Smid and Szwarc. The factors affecting the respective rate constants are discussed.

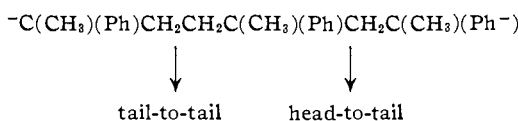
In recent studies, Vrancken, Smid and Szwarc¹ demonstrated that the equilibrium constant of the system α -methylstyrene-living poly- α -methylstyrene depends on the structure of the polymer. For example, the equilibrium constant of the process



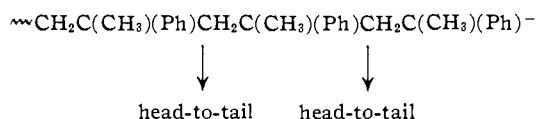
is substantially larger than that for the growth of an ordinary high molecular weight n -mer. It was shown that the variations in the equilibrium constants arise from differences in the linkages which connect the penultimate unit of the final product with the other segments of the polymer. Thus, the living dimer of α -methylstyrene has the structure²



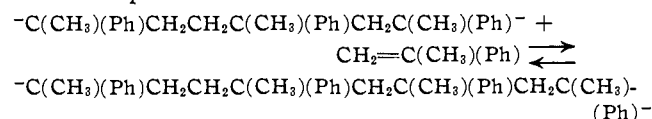
and on addition of the monomer, its terminal unit becomes sandwiched between two α -methylstyrene segments linked in a tail-to-tail and head-to-tail fashion, *i.e.*



On the other hand, in the ordinary head-to-tail polymerization the last unit of a long n -mer becomes flanked by two segments linked in a head-to-tail way when an $n + 1$ -mer is formed, namely



The strain caused by the latter type of linkages is substantially larger than that resulting from the tail-to-tail-head-to-tail array, and this accounts for the reported results. In fact, Vrancken, *et al.*,¹ have shown that the equilibrium constant of the reaction



differs insignificantly from that characterizing the high-molecular weight polymerization where head-to-tail linkages are continuously formed. The extent to which these factors affect the equilibrium constants is illustrated by the data collected in Table I.

TABLE I

COMPARISON OF EQUILIBRIUM CONSTANTS IN TETRAHYDROFURAN^a

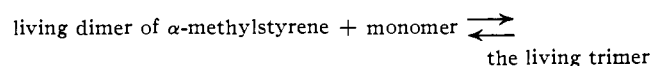
$$-(\alpha\text{MeS})_2^- + \alpha\text{MeS} \rightleftharpoons -(\alpha\text{MeS})_3^-; K_2$$

$$(\alpha\text{MeS})_n^- + \alpha\text{MeS} \rightleftharpoons (\alpha\text{MeS})_{n+1}^-; K_\infty \text{ for large } n$$

$T, ^\circ\text{C.}$	$K_2, \text{ l./mole counter-ion } K^+$	$K_\infty, \text{ l./mole counter-ion } Na^+$
-15	1750 \pm 300	3.3
0	750 \pm 100	1.35
+10	450 \pm 50	0.9
+25	240 \pm 30	0.41

^a Data taken from ref. 1.

The increase in the equilibrium constant of propagation implies an increase in the propagation rate constant or a decrease in the depropagation rate constant, or both. The work reported in this paper was carried out in order to shed light on these problems and, with this goal in mind, we investigated the kinetics of the reversible reaction



(1) A. Vrancken, J. Smid and M. Szwarc, *Trans. Faraday Soc.*, **58**, 2036 (1962).

(2) C. E. Frank, *et al.*, *J. Org. Chem.*, **26**, 307 (1961).