NaLS solutions were spread on these solutions and the per cent. decrease of the film area in ten minutes at 10 dynes per centimeter pressure noted. The results of this study are shown in Fig. 1. Evidently, above a concentration of about 30% ammonium sulfate spread films of NaLS are stable at 10 dynes film pressure.

Results

Figure 2 shows the plot of the area of the spread films at 10 dynes per centimeter film pressure per milligram of detergent plus protein against the weight fraction of detergent.

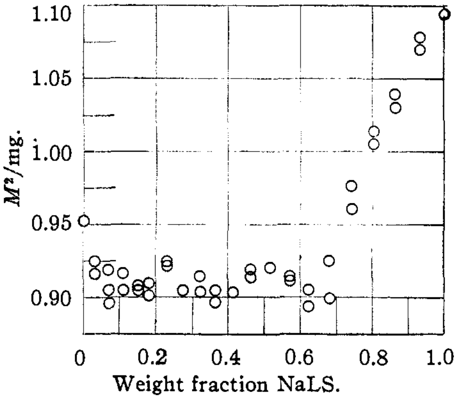

Fig. 2.—Area of the spread film in square meters per milligram at 10 dynes per centimeter of film pressure against the weight fraction of NaLS.

Discussion

Treating the results of this study in the same way as was described for mixed films of egg albumin and detergent,[1] we can calculate the number of detergent molecules bound per molecule of protein. The results of these calculations based on a molecular weight of 35,000 for β-lactoglobulin[2] are shown in Fig. 3.

There is an inflection in the curve (Fig. 3) at about 8 molecules of NaLS per molecule of protein molecule and the curve shows a decided break at about 40 detergent molecules per protein molecule. On the basis of a molecular weight of 35,000 the sum of the positive groups in β-lactoglobulin (histidine, lysine, and arginine) is about 37.[3] It seems probable that the curve shown in Fig. 3 is in reality a titration curve for the basic groups by the anionic detergent.

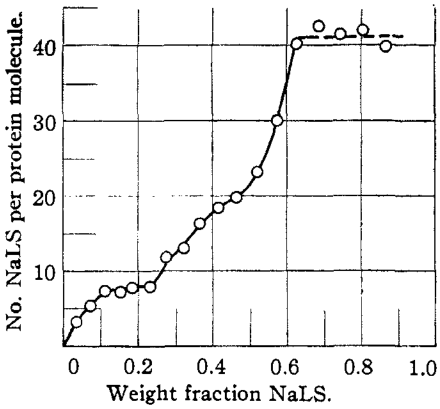

Fig. 3.—Number of NaLS molecules bound per protein molecule as a function of the weight fraction of NaLS.

Summary

1. The film areas of mixtures of β-lactoglobulin and sodium lauryl sulfate spread on 35% $(NH_4)_2SO_4$ and at 10 dynes per centimeter film pressure have been reported.

2. The number of molecules of sodium lauryl sulfate bound per β-lactoglobulin molecule has been calculated and plotted as a function of the concentration of detergent.

(3) Brand, Saidel, Goldwater, Kassel and Ryan, This Journal, 67, 1524 (1945).

Chicago, Illinois Received December 19, 1945

[Contribution from Mellon Institute of Industrial Research]

The Structure of Ethylene Polysulfides[1,2]

By Harry E. Westlake, Jr., M. Glenn Mayberry, Maurice H. Whitlock, James R. West and George J. Haddad

Armstrong, Little and Doak[3] have isolated and identified as monosulfides some of the light products from the reaction of sulfur with certain higher olefins and have described the formation of unidentified polymeric compounds. Earlier Friedman[4] obtained sulfides from the reaction of sulfur with butylene. Ethylene, the simplest unsaturated compound, seems to have been largely neglected. Victor Meyer[5] mentioned its reaction with sulfur at 300° to give a trace of thiophene, and Jones and Reid[6] found that hydrogen sulfide and ethyl mercaptan were formed at 325°. Meyer and Hohenemser[7] reported no reaction at 140°. We have found, however, that extensive reaction occurs at temperatures above the melting point of sulfur.

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(1) Contribution from the multiple industrial fellowship sustained at Mellon Institute by the Texas Gulf Sulphur Company, New York, N. Y.

(2) Presented before the Division of Organic Chemistry at the 108th meeting of the American Chemical Society, New York, N. Y., Sept. 14, 1944.

(3) Armstrong, Little and Doak, *Ind. Eng. Chem.*, **36**, 628 (1944); *Rubber Chem. Tech.*, **17**, 788 (1944).

(4) Friedman, *Petroleum*, **11**, 693 (1916).

(5) Victor Meyer, "Die Thiophengruppe," Braunschweig, Germany, 1888, p. 16.

(6) Jones and Reid, This Journal, **60**, 2452 (1938).

(7) Meyer and Hohenemser, *Helv. Chim. Acta*, **18**, 1061 (1935).

Experimental

Ethylene reacted with molten sulfur at atmospheric pressure to give a detectable product within twenty-four hours. Higher yields were obtained where pressure and solvents were used. In Table I are listed some of the experimental details for reaction in an unstirred, electrically heated autoclave. Empirically, a rise in temperature caused a rise in yield and a change in the ratio of soluble to insoluble products. Free sulfur was always observed in the final reaction mixture from these runs. In pilot plant operation, the data in the table were confirmed. However, at 165–176° all the sulfur charged to the autoclave was converted to *soluble* ethylene polysulfide, no insoluble products being formed, and no residual free sulfur remaining. An increase in time caused a much larger increase in yield of insoluble products than in soluble ones. In pilot plant operation, the xylene solution was reused repeatedly without any increase in the concentration of soluble products, although large yields of insoluble material were obtained from each run. This finding indicated that the insoluble product was a polymer of the soluble product. Numerous catalysts were tested in the reaction with completely negative results. The only materials to affect the rate of reaction appear to be the products, for Brown,[8] in a separate investigation on countercurrent absorption in a packed tower, has demonstrated that the rate of absorption of ethylene in sulfur is increased by the presence of the reaction products.

TABLE I

REACTION OF SULFUR WITH ETHYLENE IN XYLENE SOLUTION

Reaction mixture		Reaction conditions				Products	
Sulfur, g.	Xylene, cc.	Time, hr.	Temp. range, °C.	Pressure range, p. s. i. g. Start	Finish	Soluble in xylene, g.	Insoluble in xylene, g.
200	300	24	130–135	140	110	83.7	63.8
200	300	24	135–140	160	110	83.5	77.2
200	300	24	140–145	152	37	255.9	2.7
1000	1200	26	124–133	160	140	44.9	7.7
1000	1200	48	127–137	165	135	78.1	80.0
1000	1200	73	127–133	150	90	147.2	255.3

Isolation of the Products.—Where ethylene reacted under pressure with molten sulfur, the product was a solution of various olefin sulfides in sulfur. Where the reaction was carried out with a xylene solution of sulfur under pressure below 160°, the reaction mixture separated into two layers: the bottom layer was a sulfur solution of ethylene sulfides, and the top layer consisted of a xylene solution of the lower molecular weight, soluble products. Reaction in xylene solution under pressure at about 180° converted all the sulfur in the vessel to soluble, low molecular weight sulfides. A similar solution of these soluble sulfides could be obtained by continuous or batch extraction of the sulfur solutions of ethylene polysulfides formed in some of the reaction mixtures, as described above, using xylene at 120–140°. The residues from such extractions were polymeric elastomers.

Whether the xylene solution of the soluble sulfides was formed directly in the reaction mixture or by extraction, the soluble sulfides could be isolated by evaporating the solvent. If no free sulfur was present, this separation could be done by steam distillation. In the presence of free sulfur, the evaporation had to be done in stages in order to freeze out the sulfur at each step. Either process gave a red viscous oil. About 7 to 15% of this product was found to be volatile. Direct distillation, even under reduced pressure, caused almost complete pyrolysis of the non-volatile product. Therefore, steam distillation was generally used to isolate the volatile products without destroying the rest. The volatile product was a yellow to reddish orange colored liquid which possessed an evil odor and was miscible with all the usual organic solvents.

TABLE II

GENERAL CHEMICAL CHARACTERISTICS OF ETHYLENE POLYSULFIDES

	Volatile liquid	Non-volatile liquid	Polymer
Sulfur content (5)	59.46	74.2	84–89
Average molecular weight	144	462	...
Solubility in organic solvents	Soluble	CS_2 of aromatics only	None
Refractive index, $n^{20}D$	1.5746	...	...
Reaction with			
$KMnO_4$	Decolorized	Decolorized	...
Br_2	Absorbed, HBr ↑	Negligible	...
$Pb(C_2H_3O_2)_2$	PbS ↓	PbS ↓	...
Ethyl bromide	...	No reaction	...
Reduction (Zn + HCl, Al + NaOH, Na_2S)	No reaction	No reaction	No reaction

Oxidation with Nitric Acid.—A sample of the liquid, nonvolatile product (7.0 g.) was oxidized with 50 cc. of fuming nitric acid. After the violent reaction, the mixture was diluted with water and heated on a steam-bath for days to remove the nitric acid, the liquid level being maintained by additions of water. Saturation with basic lead carbonate removed sulfate ion as the lead salt, which was separated by filtration. Treatment of the filtrate with hydrogen sulfide removed the lead, and evaporation of the filtrate gave 1.0 g. of ethane disulfonic acid (m. p. 98–100°), which was confirmed by conversion to the disulfonyl chloride (m. p. 89.5–90.5°). Similar treatment of the polymeric product also gave a small yield of ethane disulfonic acid.

Oxidation with Aqueous Chlorine.—Chlorine gas was passed for an hour into a mixture of 2 g. of the volatile liquid, 10 g. of glacial acetic acid and 2.5 cc. of water according to the method of Lee and Dougherty.[9] The solution was filtered into three times its volume of water and the mixture was extracted with ether. The extract yielded about 2 cc. of a pungent liquid, 1.7 cc. of which distilled at 170–200°. Odor and boiling point identified it as β-chloroethylsulfonyl chloride, confirmed by conversion to the ammonium salt of the sulfonic acid (m. p. 188–192°). A trace of ethane disulfonyl chloride was found on the filter paper through which the reaction mixture was poured, identified by melting point (88–91°) and a mixed melting point. As ethane disulfonyl chloride decomposes at 160°, a second crude product was distilled under reduced pressure, heated by an oil-bath whose temperature was kept below 155°. Since chloroethylsulfonyl chloride was again obtained, it must be the primary product. Similar oxidation of the non-volatile liquid also yielded β-chloroethylsulfonyl chloride, together with a rubbery polymer.

Reaction with Alkali.—The volatile liquid dissolved slightly in about 1 *N* alkali upon heating. The nonvolatile liquid could be slowly but completely dissolved by refluxing with alkali of about the same normality. Undissolved portions showed no diminution in sulfur content. Acidification precipitated an oil resembling the starting material.

A suspension of about 450 g. of the polymeric ethylene polysulfide in 1 liter of an aqueous 0.8 *M* magnesium hydroxide solution containing 1.2 moles of sodium hydroxide was refluxed for forty-two hours with 310 g. of additional sodium hydroxide and filtered. The filtrate was treated with batches of 30% hydrogen peroxide until the solution became colorless. The white precipitate which appeared (8 g.) was filtered. Its sulfur content corresponded to the formula $[(C_2H_4)_3S_4]_x$ and its m. p. was 109–112°. By ex-

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[8] W. Brown, *Bull. Univ. of Pittsburgh*, **39**, 73 (1943)

[9] Lee and Dougherty, *J. Org. Chem.*, **5**, 81 (1940).

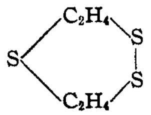
tracting with benzene and fractionally precipitating the dissolved material by evaporation, and by dilution with alcohol, a series of fractions was obtained which varied in melting point from 75 to 117° and in sulfur content from 58.7 to 66.6%. Five grams of the unfractionated product was suspended in 100 cc. of absolute alcohol and refluxed with sodium amalgam. The mixture was filtered and dry hydrogen chloride was passed through the filtrate. Filtration of the sodium chloride and evaporation of the alcohol yielded about 2.5 g. of yellowish red oil which gave a strong mercaptan test, appeared to be slightly soluble in water and very soluble in alkali. It possessed a refractive index of $n^{26}{}_D$ 1.6222 and a density of $d^{25}{}_{25}$ 1.431. It polymerized to a waxy solid when distillation was attempted. Oxidation with bromine gave a white solid (m. p. 130–132°) and the mercury mercaptide melted at 142–150°.

Discussion

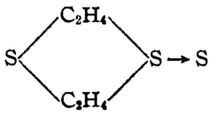
The analysis and molecular weight of the volatile polysulfide correspond to an empirical formula of $(C_2H_4)_2S_3$. The lead acetate test[10] indicated the presence of a labile sulfur atom. The inertness to alkali seemed to exclude the presence of a mercaptan group. Reaction with bromine gave a liquid product instead of the solid polymer to be expected of a dimercaptan. These observations appear to rule out the first of the three possible ways in which two ethylene groups and three sulfur atoms can be joined together

(A) $HS—C_2H_4—S—C_2H_4—SH$

(B)



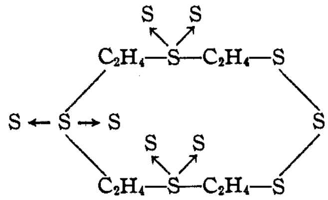
(C)



Solution in hot alkali indicates (B) since disulfides are split by this treatment,[11] but the labile sulfur test favors (C). Oxidation with aqueous chlorine gave β-chloroethylsulfonyl chloride and a trace of ethane disulfonyl chloride, definitely confirming the presence of at least one monosulfide link, for polysulfides could give only disulfonyl chlorides. Formula (B) would be expected to form equal quantities of the two products, but (C) should give almost entirely chloroethylsulfonyl chloride with only traces of ethane disulfonyl chloride. The first step, opening the ring, would produce a shift of electron density around the middle sulfur atom which would weaken one sulfur carbon bond and cause preferential splitting to chloroethylsulfonyl chloride.

As diethylene disulfide is known, treatment of the volatile product with lead acetate should have given it. Neither this reaction nor the converse synthesis of the oil from $(C_2H_4)_2S_2$ was experimentally successful. The polysulfide should be either (B) or (C) unless the assumption is false that ethylene and sulfur had combined without loss of hydrogen. This assumption is based on the fact that neither hydrogen sulfide nor the by-products expected therefrom (*e. g.*, diethyl sulfide) were ever isolated except in very minute traces where the reaction was run at 175°. Oxidation evidence favors (C), but in view of the other evidence (B) cannot be excluded.

The average molecular formula of the non-volatile liquid was $(C_2H_4S_3)_4$. The failure of all reducing agents to attack it is presumptive evidence that all the ethylene groups were joined through monosulfide linkages. This inference was confirmed by oxidation. Although fuming nitric acid produced ethane disulfonic acid, at no time was the amount isolated sufficient to account for even half the carbon known to be present. Oxidation with aqueous chlorine gave β-chloroethylsulfonyl chloride. The presence of a polysulfide group anywhere in the chain would have yielded ethylene dimercaptan or bis-mercaptoethyl sulfide (A) on reduction and a good yield of ethane disulfonyl chloride or disulfonic acid on oxidation. The only clue to the identification of the end groups is the solubility of the oil in alkali. This observation suggests mercaptan groups, unreconcilable with the fact that the liquid polysulfide could only be polymerized by heating with concentrated sulfuric acid or by direct heating for a period of months. On the other hand, Schöberl and co-workers[11] have shown that a disulfide linkage can be split by alkali. We therefore postulate that the ethylene sulfide chain is cyclized through a polysulfide group and that the monosulfide linkages are saturated with labile sulfur atoms.



The xylene-insoluble, polymeric ethylene sulfide was also soluble in strong alkali, but, unlike the liquid ethylene polysulfide, an oil mixed with sulfur instead of the original material was obtained upon acidification. This finding indicated that the polymer consisted of unknown radicals joined through polysulfide groups which were split by the alkali. The oxidation of the alkali-formed mercaptides to a polymeric disulfide of composition $(C_2H_4)_3S_4$, which could be fractionated to samples of varying sulfur content, suggested heterogeneity, that the unknown radicals were varying numbers of ethylene groups linked through monosulfide linkages. The polymeric disulfide was reduced to a mixture of mercaptans which resisted identification. Because the liquid ethylene polysulfide could be polymerized to an elastomer resembling the polymeric polysulfide, and because evidence from the study of the reaction indicated that the latter was a polymer of the former, it is believed that the polymeric polysulfide is a long chain of ethylene groups linked through monosulfide and occasionally random

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(10) Baroni, *Atti Accad. Lincei*, **11**, 905 (1930).

(11) Schöberl, *Ann.*, **507**, 111 (1933); Schöberl, Berninger and Harren, *Ber.*, **67B**, 1545 (1934); Schöberl and Eck, *Ann.*, **522**, 97 (1936); Schöberl, *Ber.*, **69B**, 1955 (1936).

polysulfide linkages, possibly cyclized, with all sulfides saturated by labile, dative-bonded sulfur atoms.

Since circumstances beyond our control have caused the complete cessation of work on this problem, proof of the structures of these products is lacking. We feel nevertheless that our results and conclusions will be of value in the literature.

Acknowledgment.—We wish to thank the Texas Gulf Sulphur Company for permission to publish these results. We are grateful to W. W. Duecker of Texas Gulf Sulphur Company and to L. H. Cretcher and W. A. Hamor of Mellon Institute for their help and advice in the research.

Summary

1. Ethylene reacted with sulfur with or without solvents or pressure to form a xylene-insoluble polymer and a soluble oil, part of which was volatile.

2. The various products were investigated and structures were postulated from the experimental evidence.

PITTSBURGH, PA. RECEIVED NOVEMBER 13, 1945

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, SOILS AND AGRICULTURAL ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

Molecular Rearrangement of Fluorylidene Dimethyl Sulfide to Fluorene-1-dimethyl Sulfide[1]

BY LOUIS A. PINCK AND GUIDO E. HILBERT[2]

The work of Ingold and Jessop[3] on the preparation of the unstable fluorylidene dimethyl sulfide (II) was repeated and their finding was confirmed. We have found that II rearranges in an alkaline medium such as liquid ammonia or alcoholic sodium hydroxide to fluorene-1-dimethyl sulfide (III). Reactions were carried with III involving graded oxidations, reduction and substitutions. The structure of the rearranged product was definitely established by comparing fluorenone-1-carboxylic acid (V), an oxidation product of III, with an authentic specimen obtained by the oxidation of fluoranthene.

The various compounds obtained in this study are indicated by the reaction chart.

Experimental

Rearrangement of Fluorylidene Dimethyl Sulfide (II).—A sealed glass tube containing 25 g. of I[3] and 75 cc. of liquid ammonia was kept in a steel bomb at room temperature for two weeks. After evaporating the ammonia the orange-colored solid was washed free from ammonium bromide and dried, m. p. 71–75°. It was distilled at 180–190° at 2 mm. pressure and then crystallized from 95% ethyl alcohol as white colorless needles, m. p. 77.5°,[4] yield 15.5 g. or 76.4%. The residue was a red resin.

Anal. Calcd. for $C_{15}H_{14}S$: C, 79.59; H, 6.24; S, 14.18; mol. wt., 226. Found: C, 79.31; H, 6.21; S, 14.25; mol. wt., 226, 220.

Fluorene-1-dimethyl sulfide (III) is fairly soluble in alcohol, very soluble in ether and is exceedingly stable thermally. Decomposition was effected by heating above 400° forming dimethyl sulfide and a dark brown resin.

Rearrangement was also obtained by the use of alkali but here the yield was only 28.3%. The following procedure was used. A solution of 13.5 g. of I in 180 cc. of water was treated rapidly with 100 cc. of a 30% solution of sodium hydroxide at room temperature, thereby depositing a practically colorless, finely divided precipitate. The mixture was well shaken for a few minutes and then rapidly filtered in subdued light and the solid was dried by rubbing it on a porous plate. It changed color very rapidly, first turning gray then bluish gray and finally to a permanganate-like color. It was rapidly washed into a flask with 125 cc. of absolute alcohol and treated with a solution of 35 g. of sodium hydroxide in 175 cc. of 60% alcohol. The mixture was shaken well and after keeping it in the dark for an hour it was gradually warmed to 45° in a course of two hours. With the exception of a red resin all of the solid went into solution, the latter also was red. The solution was diluted with water and extracted with benzene. The benzene soluble fraction was distilled at reduced pressure yielding 4.28 g. of impure distillate, leaving behind the major portion as a red resin. The distillate upon recrystallization from alcohol yielded 2.8 g. of III. The alcohol soluble residue was sublimed *in vacuo*, yielding 1.1 g. of yellow solid which upon further purification was identified as fluorenone.

Alcoholysis of Fluorene-1-dimethyl Sulfide (III).—A solution of 0.5 g. of III in about 15 cc. of methyl alcoholic hydrogen chloride was heated in a bomb tube at 125° for four days. Considerable pressure and a strong odor of mercaptan were noted upon opening the tube. The residue obtained upon the evaporation of the solvent melted at 56°, was purified by crystallizing it from methyl alcohol and then by sublimation, colorless needles, m. p. 58°, yield 65%. IV turned pale pink on exposure to light and became colorless when kept in the dark. It gave a negative test for sulfur by the sodium fusion method.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.71; H, 6.71. Found: C, 85.92; H. 6.81.

Oxidation of III.—To a hot solution of 2 g. of III in 25 cc. of glacial acetic acid was slowly added 10 g. of sodium dichromate. The mixture was heated under reflux for four hours, then cooled, diluted with water, and the precipitate which deposited was removed, weight 1.45 g., m. p. 149–158°. It was dissolved in hot benzene and extracted with dilute alkali. The extract was filtered and V was precipitated by acidifying the solution, weight 0.47 g. Orange-colored needles were obtained by crystallization from benzene, m. p. 197°; mixed melting point with a specimen of fluorenone-1-carboxylic acid obtained by the oxidation of fluoranthene[5] 196–197°.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.98; H, 3.60. Found: C, 75.05; H, 3.60.

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[1] A summary of this investigation had previously been reported by Hilbert and Pinck, THIS JOURNAL, **60**, 494 (1938).

[2] Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois.

[3] Ingold and Jessop, *J. Chem. Soc.*, 713 (1930); see also Hughes and Kuriyan, *ibid.*, 1609 (1935).

[4] All melting points are corrected.

[5] Fieser and Seligman, THIS JOURNAL, **57**, 2175 (1935).