

promote both activities, have not been made to lose entirely the reproductive element, thus indicating that the influence of the nutrients in affecting the ratio of vegetation to reproduction is quantitative and not qualitative.

On the other hand, the hypothesis of the existence of but a single vitamine for *Sclerotinia* is more plausible, according to much of the experimental evidence. It is very probable that reproduction in *Sclerotinia* is simply a different manifestation of the same activities as characterize vegetation. The single activity that is apparently most dependent on a vitamine supply is respiration. Respiration is common to all the materials which have yielded the vitamine; and the degree of metabolic, and hence respiratory, activity in these materials is proportional to the activity of the vitamine prepared from them. Thus the evidence is accumulating in favor of the view that there is a close connection between respiration in a cell and its vitamine content, and also its vitamine requirement. Just which cells in the plant world can synthesize this vitamine is still an open question. The *Sclerotinia* vitamine is possibly identical with the water-soluble B of the higher animals; and since the latter cannot synthesize this vitamine, it becomes an important point to know which plant organs can.

ST PAUL, MINNESOTA.

THE MECHANISM OF THE REACTION BETWEEN ETHYLENE AND SULFUR CHLORIDE.¹

BY J. B. CONANT, E. B. HARTSHORN AND G. O. RICHARDSON.

Received December 18, 1919.

I. Introduction.²

When ethylene gas is led into rapidly agitated sulfur monochloride at a temperature of 40° to 60°, β,β -dichloro-ethylsulfide and sulfur are formed. This may be represented by the following equation:



The following mechanisms of the reaction are possible: (1) the reaction may take place by the simultaneous action of two molecules of ethylene and one of sulfur monochloride; (2) one molecule of sulfur monochloride may react with one molecule of ethylene to give the intermediate compound $\text{CH}_2\text{ClCH}_2\text{S}_2\text{Cl}$, which then may react further with ethylene to give dichloro-ethylsulfide and sulfur, or a disulfide, $(\text{CH}_2\text{ClCH}_2)_2\text{S}_2$,

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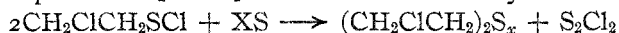
² The work presented in this paper was incidental to an investigation of an important war problem. As other matters were of greater moment, an exhaustive study of the mechanism of this reaction was impossible. It is believed, however, that the present incomplete results are of sufficient interest to warrant publication. An investigation of the same general problem from a different angle is planned.

may be formed which subsequently loses sulfur to yield the sulfide; (3) an intermediate compound, $\text{CH}_2\text{ClCH}_2\text{SCl}$, and sulfur may be the first products of the reaction; this intermediate may then unite with more ethylene. It is evident that if the speeds of the 2 successive reactions, suggested in (2) and (3), are equal throughout the reaction, the conditions will be experimentally those represented by (1), but if the speeds are different, an intermediate compound will be present in varying amounts during the reaction.

It has been possible to show by freezing-point determinations that the reaction does proceed in two stages. However, it has been found difficult to obtain conclusive evidence as to the exact structure of the intermediate product. A study of the reaction between sulfur dichloride and ethylene has thrown some light on this point. Further evidence has also been obtained from a study of the by-products of the sulfur monochloride reaction.

Sulfur dichloride combines rapidly with one molecule of ethylene and the product is apparently $\text{CH}_2\text{ClCH}_2\text{SCl}$. This is an unstable substance which combines further with ethylene producing some dichloroethylsulfide. It easily decomposes on warming, producing thick, black oils and hydrogen chloride. This decomposition is accelerated by metals and metallic salts. If the reaction between ethylene and sulfur monochloride is stopped when about half completed, the product behaves in exactly the same manner. It also decomposes into hydrogen chloride and high boiling substances. It thus seems probable that the intermediate compounds are the same in the case of both sulfur dichloride and sulfur monochloride.

The intermediate substance $\text{CH}_2\text{ClCH}_2\text{SCl}$ reacts with sulfur on warming and produces some complex sulfur compounds as the sulfur disappears. An examination of the by-products from the sulfur monochloride reaction has shown that they are polysulfides. The formation of these compounds we believe to be due to the interaction of the intermediate compound $\text{CH}_2\text{ClCH}_2\text{SCl}$ and the elementary sulfur.



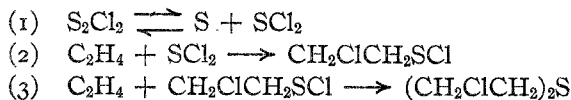
An analogous reaction is reported as taking place when CCl_3SCl is heated with sulfur; $\text{C}_2\text{Cl}_6\text{S}_3$ and $\text{C}_2\text{Cl}_6\text{S}_2$ are among the products.¹

Under certain conditions the final product of the monochloride reaction is a clear, yellow, liquid containing no precipitated sulfur. All the sulfur set free in the reaction is held in colloidal solution. The sulfur slowly separates from this solution on standing or may be quickly thrown down by warming for a few hours at 110° – 120° . *The freezing point of the material is not changed by the precipitation of the sulfur.* This clearly shows that the sulfur is present in colloidal solution. The final products

¹ Klason, *Ber.*, 20, 2378 (1887).

of the reaction are thus, dichloro-ethylsulfide, free sulfur (often in colloidal solution) and 15 to 25% of complex polysulfides.

In view of all these facts it seems that the reaction between sulfur monochloride and ethylene can be best represented by the following equations:



and a side reaction



If this mechanism is correct the ethylene reacts only with the small amount of sulfur dichloride in equilibrium with the monochloride.¹ The sulfur dichloride is continually removed by Reaction 2 and this causes Reaction 1 to go to completion. As the concentration of the intermediate compound increases it begins to react more rapidly with ethylene, according to Equation 3. This reaction only becomes appreciable when about 30% of the total ethylene has been absorbed (Fig. 3). Towards the end of the process, however, this reaction predominates as the concentration of the intermediate compound is now high and that of sulfur chloride low. The concentration of dichloro-ethylsulfide then increases rapidly until the reaction is complete.

II. Proof that the Reaction Proceeds in Two Stages. Freezing-Point Curve of Dichloro-ethylsulfide.

Pure dichloro-ethylsulfide freezes at 13.9°. The presence of impurities, of course, lowers the freezing point. This depression is approximately equal for impurities of about the same molecular weight. Fig. 1 shows a curve plotted from the results of experi-

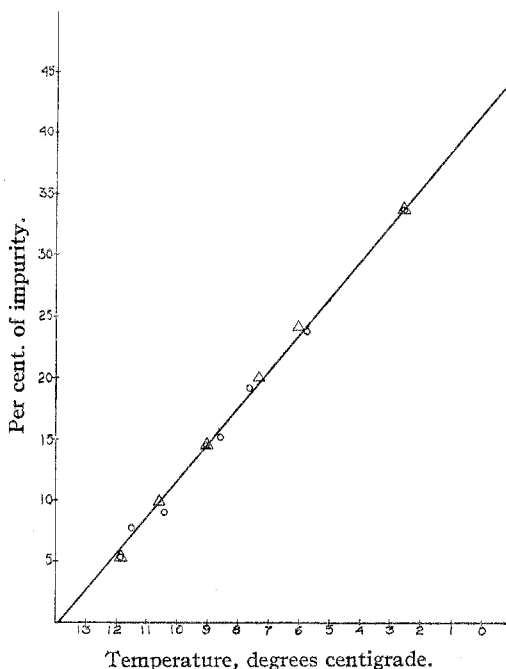


Fig. 1.

¹ There is some evidence to indicate that sulfur monochloride is in equilibrium with the dichloride and sulfur. For example, the monochloride when carefully purified is light yellow but on warming becomes a bright red which is characteristic of dilute solutions of the dichloride.

ments on the freezing point of mixtures of dichloro-ethylsulfide and carbon tetrachloride (m. w. = 154) and dichloro-ethylsulfide and trichloro-ethylsulfide (m. w. = 193). The points fall close together.

The melting-point determinations were taken in the usual form of apparatus used for determining the molecular weight by the freezing-point method. A standardized tenth-degree thermometer was used. The freezing point was always determined as the solidified mass gradually warmed up and the thermometer was read when the last portion of the solid dichloro-ethylsulfide was in equilibrium with the liquid. There was very little difficulty in obtaining consistent results with samples which did not contain more than 20% of impurity.

The curve shown in Fig. 1 easily enables one to determine the amount of any impurity in dichloro-ethylsulfide by determining the freezing point. The following table indicates the accuracy of the method. Samples containing known weights of dichloro-ethylsulfide and dichloro-propylsulfide were made up and their freezing points determined. The last two columns show the percentage composition as known from the weights of pure materials taken and as determined by the freezing point:

TABLE I.

Sample.	Freezing point. ° C.	Dichloro-propylsulfide (impurity). %.	Dichloro-propylsulfide determined from freezing point. %.
1.....	8.8	15.0	15.5
2.....	8.6	16.5	16.0
3.....	6.5	22.3	22.1
4.....	5.0	26.6	26.4

Analysis of the Reaction Mixture.

The determination of the freezing point of dichloro-ethylsulfide furnished an easy method for studying the progress of the reaction between ethylene and sulfur monochloride. Samples were withdrawn from the reaction mixture from time to time and added in known amounts to pure dichloro-ethylsulfide. The freezing point of the resulting mixture was then determined, and from the curve the per cent. of foreign material in this mixture was determined. If this per cent. was the same as the per cent. of the reaction mixture added to the pure dichloro-ethylsulfide, then the reaction mixture contained no dichloro-ethylsulfide. If it was less, then the difference was obviously due to dichloro-ethylsulfide present in the reaction mixture. Thus, by a very simple calculation, it was possible to determine how much dichloro-ethylsulfide had been formed in the reaction up to the time that the particular sample was taken. The weights of sample and pure dichloro-ethylsulfide were always taken so that a freezing point of from 5° to 9° was observed. In this range the maximum error in the determination of the percentage composition is about one part in 15. This means that the error in determining the composition

of the reaction mixture was of about the same order. The values given in the following table are, therefore, only accurate to about 10%. They, nevertheless, are entirely satisfactory in showing the progress of the reaction, and clearly show that the reaction proceeds in 2 stages.

In Table II the results of two different runs are shown. In each run about 300 g. of sulfur monochloride was used; the temperature was kept between 50 and 60°. The first column gives the per cent. of the total ethylene absorbed when the sample was taken; the second column

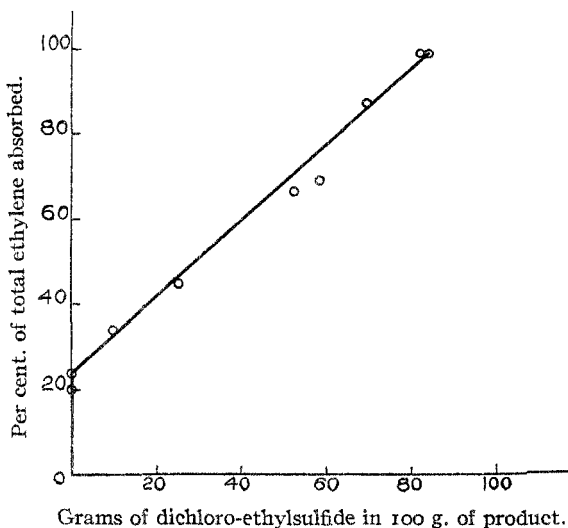


Fig. 2.

shows the number of grams of dichloro-ethylsulfide in 100 g. of this reaction mixture; the third column gives the amount which would have

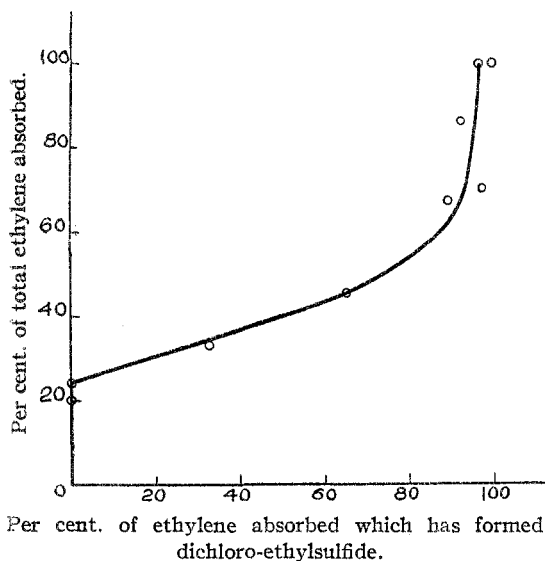


Fig. 3.

been present if all the ethylene absorbed up to that point had formed the sulfide; the fourth shows the relationship between the actual amounts of dichloro-ethylsulfide and the amount corresponding to the ethylene absorbed. Inasmuch as the theoretical amount of ethylene is never absorbed and the amount of dichloro-ethylsulfide in the final product is never 100%, the values in Col. 3 are somewhat different from the amounts based on the simple equation:



The values in Col. 2 are plotted against those in Col. 1 in Fig. 2,

the values in Col. 4 against the same variable in Fig. 3. The figures in Col. 4 obviously show what portion of the ethylene absorbed has produced dichloro-ethylsulfide.

TABLE II.

Total ethylene absorbed. %.	Dichloro-ethylsulfide in 100 g. of reaction mixture. G.	Dichloro-ethylsulfide in 100 g. if all C_2H_4 had formed the sulfide. G.	Relationship between actual dichloro-ethylsulfide and amount calculated from C_2H_4 absorbed. %.
Run I.			
19.7	0.0	16.9	0.0
34.1	9.6	29.3	32.8
70.0	58.6	59.9	97.8
100.0	82.3	85.8	95.9
Run II.			
23.8	0.0	20.6	0.0
45.0	25.5	39.1	65.2
67.25	52.6	58.4	90.1
87.5	70.1	76.0	92.2
100.0	84.9	86.9	97.7

It is evident from these results that even after 23.8% of the ethylene had been absorbed, *there was no dichloro-ethylsulfide present in the reaction mixture*. The curve shown in Fig. 3 is the most instructive, as it clearly shows the course of the reaction. Between the start and about 30% absorption an intermediate compound is being formed entirely; when its concentration has become sufficiently high, it now begins to react with ethylene to produce dichloro-ethylsulfide. By the time that 60 or 70% absorption has been reached the 2 reactions are proceeding at very nearly the same rate since the concentration of the intermediate compound is now high and that of the sulfur chloride low. The result is that during the last part of the reaction the ethylene, as fast as it is absorbed, is converted into dichloro-ethylsulfide.

III. Evidence from the Action of Sulfur Dichloride and Ethylene.

Dichloro-ethylsulfide is formed in small amounts when ethylene is bubbled through sulfur dichloride at a low temperature. The main product is a more highly chlorinated sulfide formed by the interaction of sulfur dichloride and dichloro-ethylsulfide. This side reaction can be avoided by working with dilute solutions of sulfur dichloride in carbon tetrachloride and in this way a fairly pure product can be obtained. A study of the rate of absorption of ethylene by sulfur dichloride led to the belief that this reaction proceeded in two stages. The intermediate compound can be prepared in a fairly pure state by allowing cold sulfur dichloride to come quickly in contact with an excess of ethylene.

The Intermediate Compound.

A 20-liter bottle, fitted with a manometer and a dropping funnel, was filled with ethylene. About 10 g. of sulfur dichloride (prepared accord-

ing to the method of Beckmann¹) was introduced into the bottle which was then shaken in a large ice bath for a few moments. The reaction between the dichloride and the gas was very rapid as noted by the change in the pressure. The amount of ethylene absorbed was a little less than one molecule for every molecule of sulfur dichloride. The product was a light yellow liquid which on continued agitation slowly absorbed more ethylene. Several analyses of the liquid corresponded to the formula $\text{CH}_2\text{ClCH}_2\text{SCl}$; the sulfur content averaged about 1% too low, the chlorine content about 1% too high. This indicates the presence of a somewhat more highly chlorinated impurity.

The intermediate compound was very unstable. It slowly evolved hydrogen chloride even at 0° and when warmed to 50° this evolution became rapid. At this temperature the compound was changed into a thick, black oil in the course of 3 or 4 hours. This decomposition was greatly accelerated by the presence of metallic iron or a trace of anhydrous ferric chloride. In the presence of these catalysts the decomposition was very rapid even at 5° .

The intermediate compound reacts with elementary sulfur if the two substances are warmed together for a short while. The sulfur apparently enters into the organic molecule as the product is completely soluble in 3 times its volume of carbon tetrachloride. The product is a black, thick oil which is probably a polysulfide since on oxidation with nitric acid it yields sulfuric acid and some organic sulfonic acid which was not identified. It closely resembles, in this respect, and in physical appearance, the polysulfides obtained as by-products in the monochloride reaction (see below).

Comparison of the Intermediate Compound and the Reaction Mixture Obtained from the Monochloride.

Sulfur monochloride which has absorbed *one molecule* of ethylene behaves very much like the intermediate compound prepared from sulfur dichloride and ethylene. On standing a few hours at room temperature this product rapidly gives off hydrogen chloride and passes into a thick, black oil. This decomposition is accelerated by the presence of iron and iron salts as is the decomposition of the compound $\text{CH}_2\text{ClCH}_2\text{SCl}$. Because the incomplete reaction mixture from sulfur monochloride always contains unchanged sulfur chloride and dichloro-ethylsulfide as well as an intermediate compound, no pure substance could be isolated for a more direct and convincing examination.

IV. Side Products of the Monochloride Reaction.

The amount of elementary sulfur usually formed by the action of ethylene on sulfur monochloride is only about 50% of the amount correspond-

¹ *Z. physik. Chem.*, 65, 289 (1909).

ing to the dichloro-ethylsulfide actually obtained. The yield of the dichloro-ethylsulfide based on the monochloride employed is only about 80%, although the amount of ethylene absorbed corresponds to about 95% of that theoretically required. The sulfur monochloride and ethylene which do not form dichloro-ethylsulfide are combined together with the "missing sulfur" in the form of a non-volatile organic material.

Non-Volatile Residue.

This material, which is present to the extent of 15 to 25%, is left behind in the vacuum distillation of the crude dichloro-ethylsulfide. It is a thick, black tar which often contains some elementary sulfur. The elementary sulfur can be readily separated by treating the material with carbon tetrachloride, filtering off the sulfur and evaporating the solvent. The organic material in the residue is soluble in carbon tetrachloride, benzene, chloroform and carbon disulfide; it is insoluble in ether, alcohol and water; $d_{20} 1.45$ to 1.47 . Since this black tar is completely soluble in the solvents just mentioned it must contain very little if any elementary sulfur. Judging from the amounts of ethylene and sulfur monochloride which do not appear as dichloro-ethylsulfide and the amount of sulfur unaccounted for, this material should contain 55 to 60% of sulfur and 20 to 25% of chlorine; a sample actually analyzed gave the values S = 57%, Cl = 22%. While there is every reason to believe the material contains several substances (including probably some free carbon and complex products formed at the temperature of distillation) it is nevertheless interesting to compare its composition with the formulas for various polysulfides.

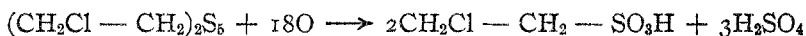
Formula:	S, %.	Cl, %.
$(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{S}_4$	50	28
$(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{S}_5$	56	25
$(\text{CH}_2\text{Cl}-\text{CH}_2)_2\text{S}_6$	60	22

It is evident that the mixture has the approximate composition of the pentasulfide. It is shown below that it is probable that the material consists very largely of this substance.

Oxidation of the Residue.

Cold conc. nitric acid readily oxidizes the material to a water-soluble product. A small amount of sulfur is left unattacked—this probably is the elementary sulfur which was present in solution in the material; it amounts to about 1%. An aqueous solution of the oxidation product contains sulfuric acid and an organic sulfonic acid containing chlorine. The sulfuric acid was removed as insoluble barium sulfate and the barium salt of the organic acid obtained in 2 experiments corresponded to a content of sulfur in the original material of 31.6 and 32.1%. If the substance were the pure pentasulfide and were oxidized according to the fol-

lowing equation, the amount of sulfur oxidized to sulfuric acid would be 34%:



The barium salt of the sulfonic acid could be recrystallized from alcohol. It contained carbon, sulfur and chlorine as well as barium. The identification of this salt was not undertaken because of the lack of time and material. It was probably the barium salt of $\text{CH}_2\text{ClCH}_2\text{SO}_3\text{H}$. The formation of sulfuric acid by the oxidation proves that the compound must contain a polysulfide linkage $-\text{S}-\text{S}-$ and the formation of an organic sulfonic acid shows the presence of the linkage $-\text{C}-\text{S}-\text{S}$. No sulfone or sulfoxide was obtained. The amount of sulfuric acid formed indicates that the material is the pentasulfide.

It is interesting to note that Guthrie¹ investigated the action of ethylene on sulfur monochloride at 100° and obtained a thick oil, d. 1.346. This material he did not purify or identify carefully but assumed it to be $\text{CH}_2\text{ClCH}_2\text{SSCH}_2\text{Cl}$ (interpreting his formulas in modern terms). Spring² repeated this experiment and oxidized the material to $\text{CH}_2\text{ClCH}_2\text{SO}_3\text{H}$ which he identified. He gives no quantitative data as to the amount of acid formed by the oxidation. Undoubtedly both Guthrie and Spring were working with a mixture of polysulfides very similar if not identical with the material we are considering. The effect of a higher temperature on the reaction between ethylene and sulfur chloride leads to blackening and the formation of a large amount of the side products.

Decomposition with Steam.

If steam is passed through the polysulfides heated to somewhat above 200° , a small amount of yellow oil gradually distils. The residue in the flask on cooling is a black, brittle mass; an analysis of it showed that it contained 62% of sulfur and 0.2% of chlorine. This material is, unlike the parent substance, only partially soluble in carbon tetrachloride. On heating in a small tube, sulfur vapors are given off in large quantities, and sulfur deposits on the walls of the tube. The material evidently contains large amounts of elementary sulfur.

The yellow oil can be distilled in vacuum, but with considerable decomposition. It has a boiling point corresponding to $170-210^\circ$ at atmospheric pressure. It is evidently a decomposition product of the original material. The analysis of two portions follow:

Low boiling fraction $170-180^\circ$ at 760 mm.

Calc. for disulfide: S, 33.5; Cl, 37.2. Found: S, 34.0; Cl, 34.4.

High boiling fraction $180-210^\circ$ at 760 mm.

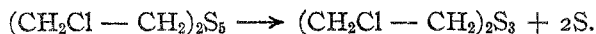
Calc. for trisulfide: S, 43.0; Cl, 31.8. Found: S, 40.7; Cl, 32.9.

On oxidation with nitric acid it yielded sulfuric acid and an organic sul-

¹ *Ann.*, 116, 234 (1860).

² *Bull. soc. chim.*, 48, 629 (1887).

fonic acid containing chlorine. A quantitative oxidation of the higher boiling material gave an amount of barium sulfate corresponding to 12% of sulfur. If the material were the trisulfide the amount would be 14.4%. The amount of sulfur left in the black, brittle residue just spoken of corresponds to 20% of the original material. If the formation of the oil followed the course of the following equation, the amount would be 22%:



It is thus certain that the oil is a polysulfide and is formed from the original polysulfide by the action of steam at a high temperature, elementary sulfur being set free. It is probably largely the trisulfide. A similar transformation has been recorded with ethyl tetrasulfide. This compound, when treated with steam at a high temperature, is said to give ethyl trisulfide and free sulfur.¹ The tetrasulfide when heated with free sulfur gives the pentasulfide. Apparently the organic polysulfides like the inorganic can take on or lose additional sulfur atoms quite readily.

Probable Constitution of the Non-Volatile Material.

All the experimental evidence given above shows clearly that the residue left after the vacuum distillation is a mixture of organic polysulfides, probably consisting largely of $(\text{CH}_2\text{Cl} - \text{CH}_2)_2\text{S}_6$. An additional piece of evidence is found in the fact that on chlorination sulfur chloride and hexachloro-ethane are formed. The following considerations show that this organic material is actually present in the crude product and is not formed during the distillation. The best crude dichloro-ethylsulfide obtained by the sulfur-monochloride process has a melting point corresponding to the presence of 10% of an impurity of a molecular weight of about 150. (The polysulfides having a much higher molecular weight would be present in larger amounts for a given melting point.) The melting point of the material is changed only a few tenths of a degree by heating the substance several hours at 120°. This shows that very little reaction takes place at this temperature. The residue from the vacuum distillation when mixed with dichloro-ethylsulfide, in the proportion in which it is obtained, lowers the freezing point to that of the original crude material. It is evident that very little if any change has taken place in the non-volatile impurity during the distillation. This evidence does not, however, rule out such a change as might take place between the polysulfides and elementary sulfur which is present to a certain extent in solution, in suspension and in "colloidal solution." The tetrasulfide might, during the vacuum distillation, take up another atom of sulfur forming the pentasulfide. This change since it does not involve the dichloro-ethylsulfide and only changes the molecular weight of the impurity about 10% would not be detected by the freezing-point methods just discussed.

¹ *J. prakt. Chem.*, [2] 15, 214 (1877).

Summary.

1. The reaction between sulfur monochloride and ethylene proceeds in two stages. The course of this reaction has been followed by a method of analysis based on freezing-point determinations.

2. It is probable that the intermediate compound is $\text{CH}_2\text{ClCH}_2\text{SCl}$. A similar intermediate product has been obtained in impure condition by the action of sulfur dichloride on ethylene.

3. 15 to 20% of non-volatile side products are always formed in the monochloride reaction. These side products are organic polysulfides.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

THE GOLD NUMBERS OF PROTALBINIC AND LYSALBINIC ACIDS.¹

BY ROSS AIKEN GORTNER.

Received December 29, 1919.

In 1902 Paal² prepared 2 substances by the action of sodium hydroxide upon egg albumin which he regarded as definite compounds. To these substances he gave the names of "protalbinic" and "lysalbinic" acids. These preparations exert a strong protective or stabilizing action when added to suspensoid sols. From the statements which occur in the textbooks one would assume the protective action of these materials to be of the highest order. Thus Freundlich³ states "Peptone solutions are so slightly colloidal that they have no protective action whatever. On the other hand, protalbinic and lysalbinic acids possess unusual ability to hold the most varied kinds of finely divided materials in colloidal solution." Taylor⁴ states, "Paal's protalbic acid and lysalbic acid are extremely active protectors," and Bechhold⁵ concludes that "Peptones have no protective action at all whereas some of the albumoses, especially *sodium lysalbinate* and *sodium protalbinate* have a very powerful protective action."

In view of these statements it appeared to be rather surprising that no exact measure of their value as protective colloids appeared in the litera-

¹ Presented before the Division of Biological Chemistry at the Cleveland meeting of the American Chemical Society, Sept. 9-13, 1918. Published with the approval of the Director as Paper No. 189, Journal Series, Minnesota Agricultural Experiment Station.

² C. Paal, *Ber.*, **35**, 2195-2206 (1902).

³ Freundlich, H. "Kapillarchemie," Leipzig, 1909, p. 451.

⁴ W. W. Taylor, "The Chemistry of Colloids," Longmans, Green & Co., N. Y., 1915, p. 130.

⁵ H. Bechhold, "Colloids in Biology and Medicine," translated by J. G. M. Bullowa, Van Nostrand Co., N. Y., 1919, p. 86.