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The Water–Formaldehyde–Hydrogen Sulfide System. I. Solubility of Hydrogen Sulfide in Aqueous Solutions of Formaldehyde and First Solid Product of the System

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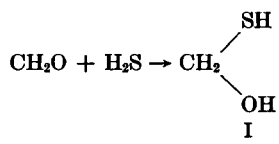
Synopsis

We have ascertained that aqueous solutions of formaldehyde absorb hydrogen sulfide proportionally to the formaldehyde present in solution. The highest molar ratio obtainable in solution is equivalent to the value $CH_2O/H_2S = 2$. When this ratio is reached, regardless of the initial concentration of formaldehyde, if the solutions are maintained constantly under pressure of hydrogen sulfide, separation of a solid product begins. Various chemical and physical studies indicate that the first solid separated from this system is $HSCH_2SCH_2SCH_2OCH_2OH$. A possible mechanism of formation of this compound from the liquid phase is discussed.

Many investigators have studied the interaction of hydrogen sulfide with aqueous solutions of formaldehyde in the presence of strong acids, which leads to formation of the cyclic trimer of thioformaldehyde (1,3,5,-trithiane).

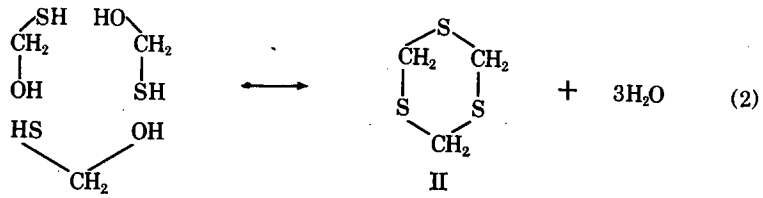
Hofman[1] first reported this reaction, while Bonst and Constable[2] described conditions leading to high yields (92–94%) of the trithiane.

Bauman[3] proposed that the intermediate I plays an important role in the reaction:



(1)

In the presence of strong acids, I may react giving trithiane (II) with elimination of three molecules of water.



Bogdanski and Chrzaszczewski[4] ascertained that the reaction proceeds essentially as proposed by Bauman and while reaction (1) is fast, reaction (2) is slow. Therefore the intermediate obtained by reaction (1) may react to form such other intermediates as $CH_2(SH)_2$ (III) and $(HOCH_2)_2S$ (IV).

We have ascertained that the reaction of hydrogen sulfide with aqueous formaldehyde, under suitable conditions[5,6] in the presence of sulfuric acid, gives rise to a polymer with a polythiomethylene structure.

On the other hand, few investigations have been carried out on the reaction of hydrogen sulfide with aqueous solutions of formaldehyde at normal pH (2.5–3.5). These investigations are summarized in the patent of Marks,[7] according to which a white solid having a sulfur content of about 51.5% and a melting point of 80°C. separates out on saturating commercial solutions of formaldehyde with hydrogen sulfide. No further data regarding the solid so precipitated and the progressive uptake of hydrogen sulfide by aqueous solutions of formaldehyde were available to date.

Therefore, it was in our purpose to study the reaction between hydrogen sulfide and aqueous solutions of formaldehyde. The conditions that give rise to the formation of a solid product were investigated and the properties of this compound determined.

RESULTS

In order to study this reaction we allowed aqueous solutions of formaldehyde (at their standard pH) to absorb hydrogen sulfide and determined the content of formaldehyde and hydrogen sulfide in the liquid phase. All our experiments were carried out in duplicate. One experiment was stopped at the point at which formation of the solid phase began. The product was filtered and its properties determined. Another experiment was carried to completion in order to permit determination of the liquid phase composition during the reaction. Further details on the method are given in the experimental section.

Table I shows the changes in composition of the liquid phase, with a starting formaldehyde concentration of 15.08 wt.-% and with continuous uptake of gaseous hydrogen sulfide.

In Figure 1 is plotted the behavior of the composition of the liquid phase from the values reported in Table I. From Table I and Figure 1 it may be seen that hydrogen sulfide is much more soluble in aqueous solutions of formaldehyde than in water; (the solubility of H_2S in H_2O at 25°C. and

TABLE I
Changes in Composition of the CH_2O–H_2O System during the Uptake of H_2S at Constant Pressure

CH_2O, wt.-% in liquid phase	H_2S, wt.-% in liquid phase
15.08	0
14.95	0.71
14.82	1.75
14.52	2.70
14.41	3.37
14.33	4.02
14.11	4.90
13.79	5.70
12.88	6.78[a]
12.47	6.50[a]
10.46	5.42[a]
8.87	4.74[a]

[a] Compositions of liquid phase determined in the presence of solid phase.

760 mm. Hg is 0.337% by weight). This significant difference in solubility is a first indication of reaction, in solution, between hydrogen sulfide and formaldehyde.

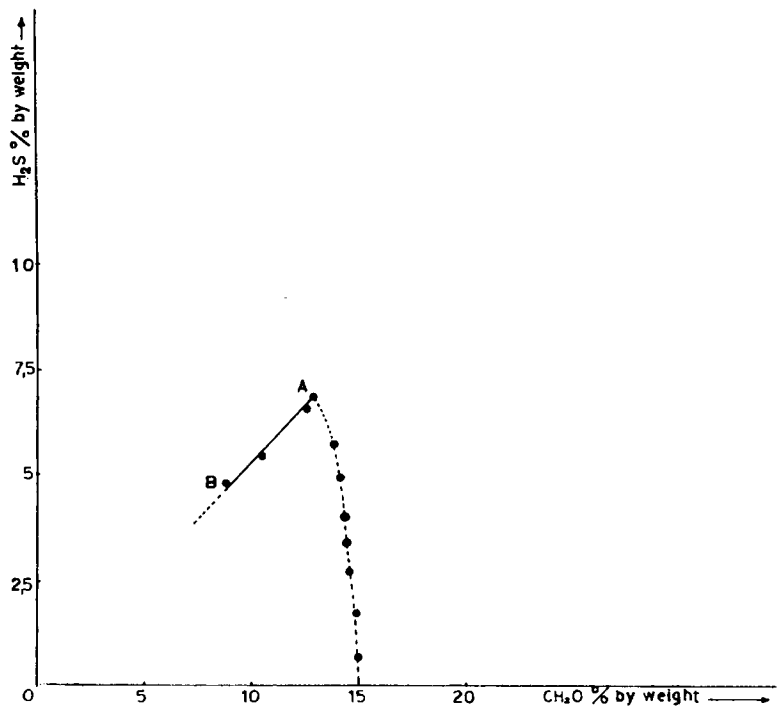


Fig. 1. Change in the composition of the CH_2O–H_2O system with uptake of H_2S. Initial CH_2O content: 15.08 wt.-%.

TABLE II
Composition Changes of the CH_2O–H_2O System with Uptake of H_2S at Constant Pressure

5.05 wt.-% initial CH_2O		10.05 wt.-% initial CH_2O		20.61 wt.-% initial CH_2O		24.89 wt.-% initial CH_2O		31.12 wt.-% initial CH_2O	
CH_2O, wt.-%	H_2S, wt.-%	CH_2O, wt.-%	H_2S, wt.-%	CH_2O, wt.-%	H_2S, wt.-%	CH_2O, wt.-%	H_2S, wt.-%	CH_2O, wt.-%	H_2S, wt.-%
5.05	—	10.05	—	20.61	—	24.89	—	31.12	—
5.04	0.37	9.91	0.92	20.52	1.03	24.62	3.21	30.94	0.62
4.92	1.14	9.55	3.00	20.19	2.07	23.59	6.55	30.59	2.52
4.48	1.89	9.30	3.67	19.91	3.33	23.19	8.04	29.79	5.91
4.26	2.13[a]	8.61	4.11	19.29	4.72	22.89	8.72	28.29	8.04
2.08	1.08[a]	7.10	3.81[a]	19.00	5.89	21.62	9.87	28.04	9.12
1.82	0.94[a]			17.81	7.52	20.68	10.27	27.61	9.79
				17.51	8.04	19.59	10.51[a]	27.10	10.70
				16.42	8.51[a]	18.72	9.70[a]	25.75	11.40
				15.60	8.00[a]			25.70	12.06
								25.65	12.42
								25.38	12.51
								24.19	12.79[a]
								23.29	12.16[a]
								22.38	11.77[a]
								21.82	11.79[a]

[a] Compositions of the liquid phase determined in the presence of solid phase.

Moreover, it may be noted that hydrogen sulfide concentration in solution reaches a maximum of 6.78%, while formaldehyde concentration decreases slightly. In connection with this maximum the separation of a white solid phase starts. When the system is kept under constant pressure of hydrogen sulfide, the relative concentrations of hydrogen sulfide and formaldehyde in the liquid phase, in the presence of solid, change according to the linear behavior AB of Figure 1.

We were unable to analyze the liquid phase in the experiment reported in Table 1, for liquid phase having a formaldehyde content lower than 8.87%, owing to the great quantity of the solid phase present.

To avoid this, we have plotted the changes in composition of the liquid phase, in presence of the solid, starting from different concentrations of formaldehyde (5.05, 10.05, 20.61, 24.89, 31.12% by weight). Table II shows the changes in compositions of the liquid phase with the various starting contents of formaldehyde.

From the values reported in Table II it may be seen that, for every solution of different initial CH_2O concentration, hydrogen sulfide reaches a maximum.

Figure 2 shows the changes in composition of CH_2O–H_2O systems with uptake of gaseous hydrogen sulfide according to the data reported in Tables I and II. The hydrogen sulfide concentration maxima are on a straight line; moreover, all points corresponding to the composition of liquid in presence of solid are on the same straight line.

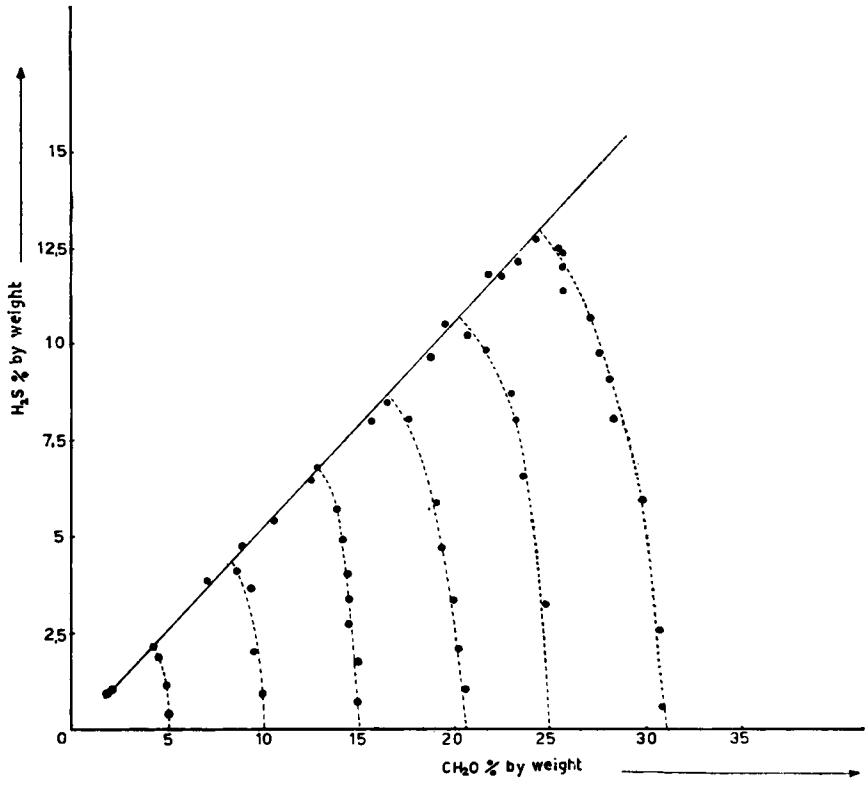


Fig. 2. Change of the composition of various CH_2O–H_2O systems with uptake of H_2S. Initial CH_2O contents: 5.05, 10.05, 15.08, 20.61, 24.89, and 31.12 wt.-%.

Regardless of the starting formaldehyde concentration of the system, the composition of the liquid phase follows the straight line in Figure 2. It is now clear that the system is more affected by the H_2S/CH_2O ratio than by the concentration of the individual components. The critical value calculated graphically is 0.54 by weight and is equivalent to a H_2S/-CH_2O molar ratio of 1/2.1.

The solids, filtered immediately as they precipitated from the saturated solutions, have been analyzed. The S content and the melting range of the solids obtained from formaldehyde solutions at different concentrations, reported in Table III, are in good agreement with each other, if it is considered that only the first solid precipitating out may not be obtained in every experiment.

For the same reason it may be seen in Figure 2 that it is not possible to determine exactly the point of contact with the straight line of Figure 2 for each starting formaldehyde concentration.

The analytical data and the melting ranges indicate that the different samples may yield the same product. Moreover, regardless of the formaldehyde concentrations these samples show the similar infrared spectra,

TABLE III
S Content and Melting Range of Solids Obtained from CH_2O Solutions with Different Initial Concentrations

Sample	CH_2O concentration in the initial solution, wt.-%	Characteristics of solids	
		S content, wt.-%	Melting range, °C.
1	5.05	53.85	105–115
2	10.05	52.67	100–105
3	15.08	51.98	98–105
4	20.61	52.39	98–112
5	24.89	53.17	102–110
6	31.12	53.20	103–108

x-ray diffraction patterns, the same extractibility with cold acetone, and the same molecular weight.

The different samples were extracted with acetone at 0°C. and the soluble portion recovered by evaporation of solvent under vacuum. In all cases we found that the percentage of soluble product is higher than 90%. Results of elementary analysis, melting range, molecular weight, and yield of the solid extracted with acetone are reported in Table IV. These characteristics are practically the same as those reported by Marks.[7]

TABLE IV
Characteristic of Products Extracted with Acetone at 0°C. from Samples 1–6 of Table III

Sample	Elementary analysis			Melting range, °C.	Molecular weight	Yield in solid product of the extraction with acetone at 0°C., % by weight
	C, %	H, %	S, %			
1	25.65	5.46	51.80	79.5–83	196	92
2	25.82	5.50	51.53	80–82	197	92
3	25.93	5.33	51.46	80.5–83	194	94
4	25.96	5.44	51.45	80–82.5	192	93
5	25.68	5.40	51.85	81–83.5	197	92
6	25.72	5.35	51.68	81–83	195	93

The elementary analysis data and the molecular weights indicate for the reaction product (V) between hydrogen sulfide and aqueous formaldehyde the empirical formula $C_4H_{10}O_2S_3$.

Infrared Analysis

In order to determine the nature of the endgroups of this compound, infrared analysis was performed before and after acetylation.

The infrared spectrum of product V (Fig. 3) shows absorption bands at 3.0 and 9.9 μ, which can be attributed to —OH and C—O stretching, re-

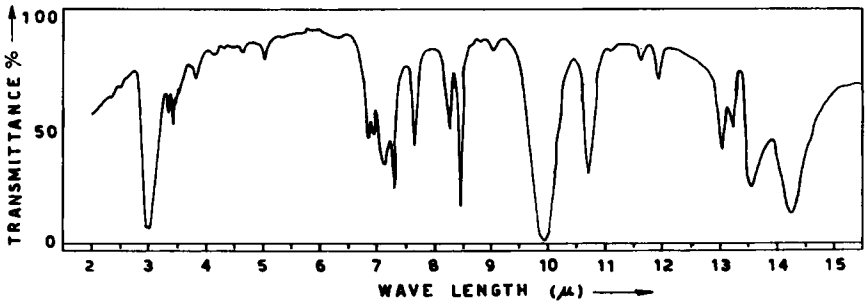


Fig. 3. Infrared spectrum of the solid product obtained from the CH_2O–H_2O–H_2S system.

spectively, of the —CH_2OH group and a band at 3.85 μ attributable to —SH stretching.

Owing to the difference between the coefficients of absorption of —OH and —SH groups of this compound at 3.0 and 3.85 μ, a quantitative evaluation of the absorption ratio between —OH and —SH stretching is very difficult; moreover, the probable presence of intermolecular hydrogen bonding also affects the same coefficients.

However, we were able to ascertain that the intensity ratio of the two bands corresponds to that of compounds with both one hydroxyl and one thiol group.

In the spectra of acetylated product (Fig. 4) the three absorption bands of hydroxyl and thiol groups disappear and new bands appear at 5.72 and 8.25 μ attributable to an —O—$COCH_3$ group, as well as bands at 5.90, 8.85, and 10.45 μ attributable to an —S—$COCH_3$ group.

The bands at 5.72 and 5.90 μ, attributable to ester and thiol ester groups, respectively, have about the same intensity.

Moreover, the values of the relative coefficients of absorption are practically the same; thus the presence of hydroxyl and thiol endgroups in the unacetylated compound is confirmed.

By infrared investigation on a warmed cell, with very mild thermal treatment, it has been ascertained that partial transformation of the acetylated product to *S*-trithiane occurs. On heating at 70°C. for 30 min. the char-

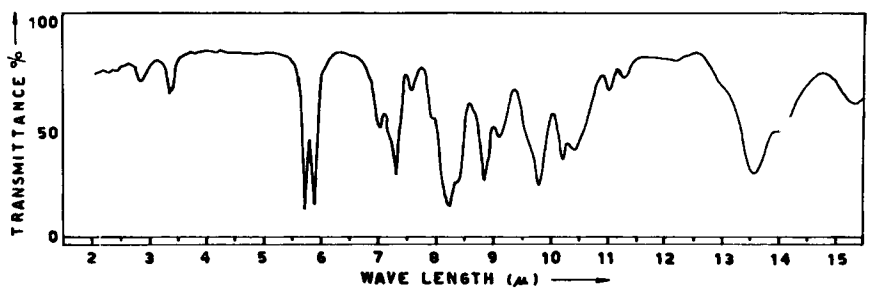


Fig. 4. Infrared spectrum of the solid product obtained from the CH_2O–H_2O–H_2S system and subsequently acetylated.

acteristic absorption bands of the acetylated product disappear and the characteristic absorption bands of *S*-trithiane appear. After 1 hr. at 105°C. the spectrum corresponds exactly to that of *S*-trithiane. In addition, some characteristic bands of polythiomethylene (at 11.3, 13.5, and 14.2 μ) and some bands of esters (at 5.7 μ) are present; these last may be due to volatile products (methylene diacetate?) because they disappear after several hours at 105°C.

X-Ray Analysis

The product gives the x-ray powder pattern reported in Figure 5*D* which was obtained by a high-angle spectrometer using CuKα radiation. It was not possible to obtain this product as a fiber or single crystal or with a preferred orientation.

It may be noted that some relation seems to exist between the patterns of precipitate and of hexagonal polythiomethylene (Fig. 5*C*); this could indicate a possible crystal lattice only slightly distorted with respect to that of hexagonal polythiomethylene. A similar situation is observed for the two crystal forms of polyoxymethylene[8,9] (Figs. 5*A* and 5*B*). As has been mentioned previously,[5] if the reaction between hydrogen sulfide and aqueous formaldehyde is carried out in the presence of sulfuric acid, the formation of the same solid precipitate takes place. On further absorption of hydrogen sulfide this first product slowly turns into polythiomethylene.

In agreement with this progressive rearrangement, the x-ray powder patterns present all the intermediate features between the pattern of our product and that of polythiomethylene (Figs. 5*C* and 5*D*).

The three reflections at 2θ (CuKα) = 20.3°, 21.1°, and 21.8° and the two reflections at 29.7° and 30.5° (Fig. 5*D*) tend to overlap, giving, eventually, the two single reflections of polythiomethylene at 2θ = 20.2° and 30.3°. As an example, Figure 5*E* shows one such pattern of an intermediate product with a sulfur content of 54.9%.

On the basis of these data, one may consider that of the five reflections mentioned above, the first three may be of the type (*hk*0) and the last two of the type (*hkl*).

However none of the differences among the values of $\sin^2 \theta$ for the three (*hk*0) reflections is equal to the differences among the corresponding values for the (*hkl*) reflections. Therefore the possibility that two of the first three reflections have the same indices *hk* of the last two and that the *z* axis is perpendicular to the *xy* plane at the same time may be excluded. The correspondence of indices *hk* may be possible only if the *z* axis is inclined with respect to the *xy* plane and a triclinic lattice is present. The same conclusion would also be reached by the assumption that the two reflexions at 2θ = 29.7° and 30.5° may be of the types (*hkl*) and ($hk\bar{l}$) with the same absolute values of the indices.

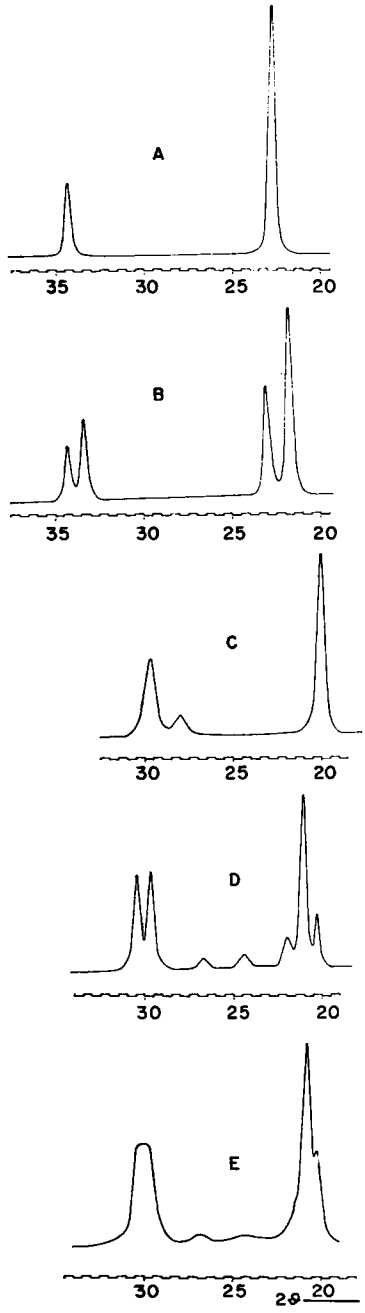


Fig. 5. Powder patterns obtained by high-angle spectrometer with CuKα radiation: (*A*) hexagonal polyoxymethylene; (*B*) orthorhombic polyoxymethylene; (*C*) hexagonal polythiomethylene; (*D*) solid product obtained by reacting hydrogen sulfide with aqueous formaldehyde; (*E*) solid product obtained by reacting hydrogen sulfide with aqueous formaldehyde in the presence of a small amount of sulfuric acid.

DISCUSSION

On the basis of general considerations of the first product of reaction between formaldehyde and hydrogen sulfide,[3,4] and from the general characteristics of infrared and x-ray spectra, the hypothesis of a linear structure with four methylenic units linked by a sulfur or an oxygen atom is quite acceptable.

The infrared spectra of extracted and acetylated product show the presence in the molecule of both hydroxyl and thiol endgroups so that only three hypothetical structural formulas, VI, VII, and VIII, remain.

$$HS—CH_2—S—CH_2—S—CH_2—O—CH_2—OH$$
VI

$$HS—CH_2—S—CH_2—O—CH_2—S—CH_2—OH$$
VII

$$HS—CH_2—O—CH_2—S—CH_2—S—CH_2—OH$$
VIII

It has been found that the acetonic extracts are soluble in water at 60°C. This dissolution is accompanied by a partial hydrolysis of the compound. For every molecule of hydrolyzed product there are two —SH endgroups and two molecules of formaldehyde which can be titrated in solution. This result may be explained only if structure VI is the correct one for the compound. This formula also agrees with the formation of *S*-trithiane during the acetylation.

The reported results show that, under the experimental conditions used, the absorption of hydrogen sulfide by the liquid phase is proportional to the quantity of formaldehyde present. When the H_2S/CH_2O ratio reaches a value of about $^1/_2$, the liquid phase is saturated and the product separated is $HS—CH_2—S—CH_2—S—CH_2—O—CH_2—OH$. The solid phase is then richer in sulfur than the liquid one. The behavior of the formaldehyde–hydrogen sulfide–water system may be represented by Figure 6, for a starting solution at 15% in formaldehyde, the uptake of hydrogen sulfide being plotted against the formaldehyde concentration in solution. The data of Table III on the solid precipitated indicate that, on the average, 0.779 mole of hydrogen sulfide* is used per mole of formaldehyde in the formation of the solid phase.

In the liquid phase in contact with this solid, 0.476 moles of hydrogen sulfide correspond, on the average, to one mole of formaldehyde. The difference, 0.779 − 0.476 = 0.303, is the number of moles of hydrogen sulfide per mole of formaldehyde which the liquid phase, already saturated with hydrogen sulfide, must absorb to give the solid phase.

This corresponds to the behavior of a straight line (Fig. 6) which, starting from the beginning of the formation of the solid phase, has a slope of

* This value was calculated by determining the thiol endgroups of samples 1–6 according to the method of Bell[10] in order to obtain the moles of CH_2O and CH_2S present in the solids for each —SH endgroup. From the average of the found values we have calculated the CH_2O/H_2S ratio for the formation of the solid.

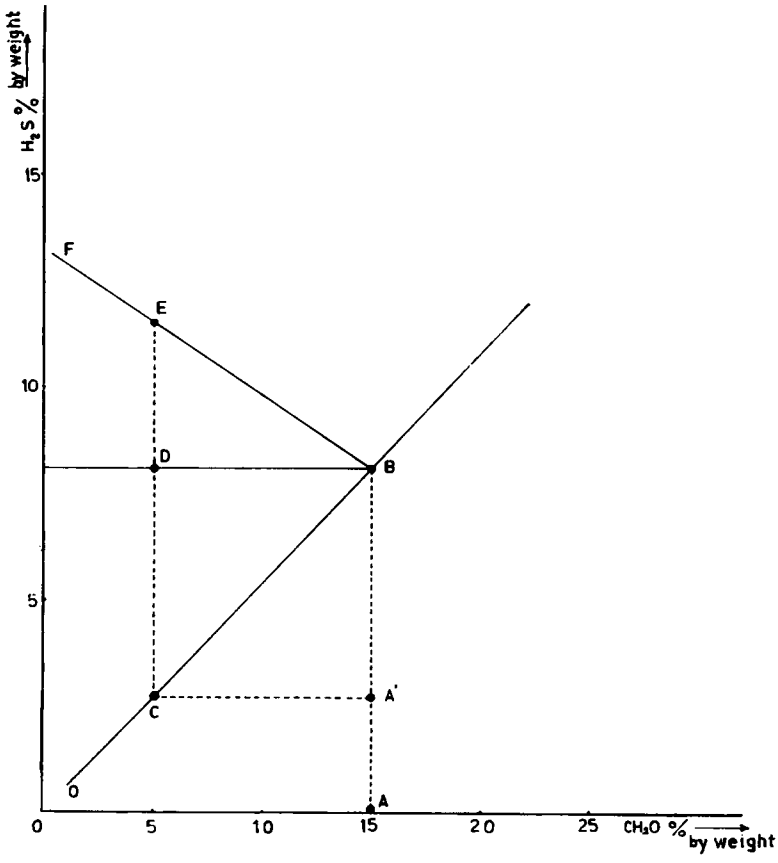


Fig. 6. Liquid phase composition of the system CH_2O–H_2O–H_2S and the quantity of CH_2O and H_2S consumed in the solid phase formation.

0.344. This value represents the uptake in grams of hydrogen sulfide per gram of formaldehyde. In the *AB* part of the curve (assumed, for the sake of simplicity, to be linear) the dissolved hydrogen sulfide reaches the composition of the liquid phase, given by the point *B*, at which the separation of the solid starts. Then the composition of the liquid phase changes according to the line BCO. The line BEF represents the total uptake of hydrogen sulfide of the system; it is related to the variation of the formaldehyde concentration in the liquid phase. To any liquid phase of composition *C* the segments *CA'* and *CE* represent, respectively, the formaldehyde and the hydrogen sulfide consumed in the solid formation. The segment *DE* represents the extra uptake of the hydrogen sulfide above that absorbed by the liquid phase at the solubility limit *B*.

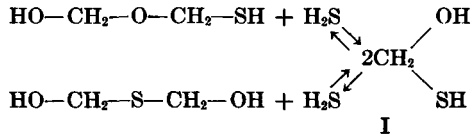
As to the reaction mechanism of the hydrogen sulfide uptake in aqueous solutions for a molar ratio $CH_2O/H_2S \simeq 2$ in the liquid phase, let us postulate the existence of a first product of addition of one mole of hydrogen sulfide to two moles formaldehyde, as shown in eq. (3).

$$H_2S + 2CH_2(OH)_2 \rightleftarrows HO{-}CH_2{-}O{-}CH_2{-}SH + 2H_2O \quad (3a)$$

$$H_2S + 2CH_2(OH)_2 \rightleftarrows HO{-}CH_2{-}S{-}CH_2{-}OH + 2H_2O \quad (3b)$$

These equilibria must be almost completely shifted toward the right, owing to the negligible solubility of hydrogen sulfide in water; reaction (3) is completed when in the solution the ratio $CH_2O/H_2S = 2$ is reached (point *B* in Fig. 6).

It may be assumed that the hydrogen sulfide subsequently absorbed reacts with the products of reaction (3) as shown in eq. (4).



(4)

The intermediate I is the same compound cited by Bauman for eq. (1). The presence of an appreciable quantity of intermediate (I) in solution would lower the ratio CH_2O/H_2S below the value (2) which is not in the presence of the solid phase. Therefore the concentration in solution of I must be very low. This intermediate may react immediately with the product of reaction (3) as shown in eqs. (5–8).

$$HO{-}CH_2{-}O{-}CH_2{-}SH + HO{-}CH_2{-}SH \rightleftharpoons HO{-}CH_2{-}O{-}CH_2{-}S{-}CH_2{-}SH + H_2O \quad (5)$$

and successively

$$HO{-}CH_2{-}O{-}CH_2{-}S{-}CH_2{-}SH + HO{-}CH_2{-}SH \rightarrow \underset{\text{IX}}{HO{-}CH_2{-}O{-}CH_2{-}S{-}CH_2{-}S{-}CH_2{-}SH} + H_2O \quad (6)$$

Alternatively:

$$HO{-}CH_2{-}S{-}CH_2{-}OH + HS{-}CH_2{-}OH \rightleftharpoons HO{-}CH_2{-}S{-}CH_2{-}S{-}CH_2{-}OH + H_2O \quad (7)$$

and successively

$$HO{-}CH_2{-}S{-}CH_2{-}S{-}CH_2{-}OH + HS{-}CH_2{-}OH \rightarrow \underset{\text{X}}{HO{-}CH_2{-}S{-}CH_2{-}S{-}CH_2{-}S{-}CH_2{-}OH} + H_2O \quad (8)$$

Of the two final products IX and X, only the IX corresponds to the structure previously postulated. Therefore it is probable that the overall process is that shown by the reactions (3a), (4), (5), and (6).

The reaction might go also according to (3b), (4), (7), and (8), but this is prevented because it leads to a final product that is certainly more soluble than the one obtained by the first series of reactions.

EXPERIMENTAL

Apparatus

The apparatus (Fig. 7) consists of two round-bottomed flasks of about 500 cc. capacity (A,B) which are connected by rubber tubing with a three-way stopcock (E) one outlet of which can be opened to the air to allow the discharge of the hydrogen sulfide.

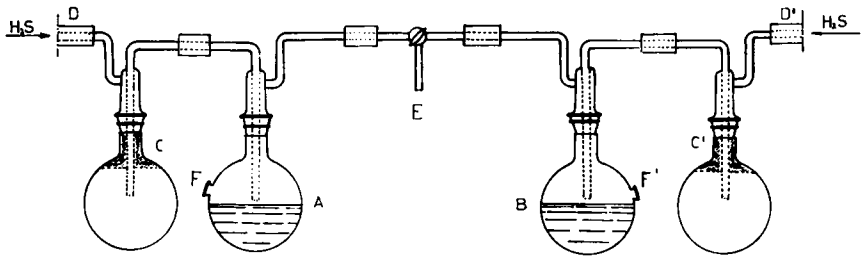


Fig. 7. Apparatus for absorption of H_2S by aqueous solutions of formaldehyde.

Hydrogen sulfide is introduced at D and D′ so that a hydrogen sulfide pressure of 760 mm. Hg is maintained in the apparatus. Between the hydrogen sulfide source and the absorbing flasks are inserted two safety flasks (C and C′) with glass wool filters. Flasks A and B contained solutions of equal formaldehyde concentration. The flasks A and B are equipped with a short sidearm (F and F′) hermetically sealed with a soft rubber stopper through which solutions may be withdrawn by means of a syringe without any change with the external atmosphere. This is a closed system and the solutions are constantly kept in a hydrogen sulfide atmosphere.

Stopcock E is opened to the atmosphere at the beginning of the experiment to permit flushing out air with H_2S. Flasks A and B are in a bath at a constant temperature of 25 ± 0.1°C.

A typical experiment is as follows. Formaldehyde solutions of the same concentration are introduced into flasks A and B. Aliquots of solution are drawn from A and the content of formaldehyde and of hydrogen sulfide is determined.

Flask B is taken from the apparatus when a determined quantity of solid precipitate is reached, and the suspension in the flask is filtered.

The time required for the formation of the precipitate depends on the experimental conditions (pressure of H_2S, stirring, temperature, etc.). Under the conditions of our experiments precipitation of the solid product began after about 10 days.

When the precipitation of the solid starts the flask B is taken from the apparatus. The suspension formed is filtered with a Büchner funnel and the solid washed with H_2O and dried at 40°C. under vacuum of 20 mm. Hg for 48 hr. This product is then characterized. The drawing of samples and the analysis of the aliquots is continued with flask A during the pre-

cipitation at the solid. In some cases the sample is a cloudy suspension; it is therefore filtered by a Schleicher and Schüll Nr. 589[2] filter paper and the clear solution analyzed in the usual way.

Formaldehyde Determination in Liquid Phase

A known quantity of solution drawn from flask A is placed in a 200 cc. volumetric flask, diluted with water containing an excess of zinc acetate, $Zn(CH_3COO)_2$, and H_2S is precipitated in this way as ZnS.

The volumetric flask is then filled to the mark. After 20 min. the suspension is filtered by a Schleicher and Schüll Nr. 589[2] filter paper. The formaldehyde is determined in the filtrate according to Romijn's method.[11]

Hydrogen Sulfide Determination in the Liquid Phase

The concentration of hydrogen sulfide in the samples drawn from flask A was determined by an iodometric method.[12]

Carius determinations of total sulfur content in solution show that the hydrogen sulfide determined by iodometric method corresponds to the total sulfur present in solution.

According to the above considerations, the hydrogen sulfide determined in solution is essentially that formed in the hydrolysis of the product of reactions (3a) and (3b). The presence in the solution of detectable quantities of the products of reactions (5–8) seems to be excluded. In fact, in the same way as occurs for the final product and for the products of reactions (3a) and (3b) the product of reactions (5–8) would give on hydrolysis $CH_2(OH)_2$ and $CH_2(SH)_2$.

$$H_2O + HO{-}CH_2{-}O{-}CH_2{-}S{-}CH_2{-}SH \rightleftharpoons 2CH_2(OH)_2 + HS{-}CH_2{-}SH$$
$$H_2O + HO{-}CH_2{-}S{-}CH_2{-}S{-}CH_2{-}OH \rightleftharpoons 2CH_2(OH)_2 + HS{-}CH_2{-}SH$$

Also in these cases two moles of formaldehyde and one mole of hydrogen sulfide, derived from two —SH endgroups of the above mentioned compound would be determined in the solution. But in this case the analysis of the total sulphur, by the Carius method would give a content of sulfur double that found by the iodometric method. Besides, when the saturation limit is reached, the detectable formaldehyde should be a third lower than the formaldehyde present at beginning of the experiment.

Total Sulfur Determination in the Solid Products

These determinations were made according to the Schöninger method.[13]

Melting Range Determination

The melting range was observed with the aid of an optical microscope.

Acetone Extraction

A portion of product was mixed with 50 parts of acetone and kept at 0°C. for 5 hr. The solution was then filtered and dried at 20°C. under vacuum.

Hydrolysis and Determination of —SH Endgroups

A weighed portion (about 0.4 g.) of product obtained from acetone extraction was placed in a 500-cc. volumetric flask.

The flask was filled with distilled water to the mark and warmed in a water bath at 60°C. until the product dissolved.

The —SH endgroup content of the solution was determined by a previously described method.[10] The formaldehyde content of the solution in a second portion was determined as previously described.

Acetylation

A 1-g. portion of the product was suspended in 50 cc. of benzene, and 3 cc. of CH_3COCl added with some Zn chips. The mixture was mixed at room temperature for 4 hr. and at the end warmed to 60°C. for several minutes until the product dissolved.

The solution so obtained was filtered and the filtrate was evaporated under vacuum at room temperature; a dense liquid was obtained which at temperatures below 20°C. begins to crystallize. This liquid, on being allowed to stand several days at room temperature, partially changes to *S*-trithiane; this transformation is accelerated by heating. There is also formation of *S*-trithiane if acetylation is carried out at higher temperature.

Molecular Weight Determination

The molecular weight determinations were made in acetone solution by a 301A Mechrolab vapor pressure osmometer.

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Résumé

On a vérifié que les solutions aqueuses de formaldéhyde absorbent de l'hydrogéne sulfuré proportionnellement à la formaldéhyde présente en solution Le plus haut rapport molaire obtenu dans cette solution équivant à la valeur $CH_2O/H_2S = 2$. Quand on

réalise ce rapport, independamment de la concentration initiale de formaldéhyde si l'on tient cette solution constamment sous une pression d'hydrogéne sulfuré, c'est alors qu'a lieu la séparation d'un produit solide. Au moyen de plusieurs recherches chimiques et physiques on a pu constater que le premier solide qui se prépare du systeme eau–formaldéhyde–hydrogéne sulfuré, c'est: $HSCH_2SCH_2SCH_2OCH_2OH$. Aussi peut-on postuler un possible mécanisme de formation de ce composé dans la phase liqueuse.

Zusammenfassung

Es wird festgestellt, dass Formaldehydlösungen eine Schwefelwasserstoffmenge absorbieren, die dem answesenden Formaldehyd proportional ist. Das grösste in der Lösung auftretende Molverhältnis beträgt $CH_2O/H_2S = 2$. Das Verhältnis ist von der Ausgangs-Formaldehydkonzentration unabhängig; hält man die Lösung unter konstantem Schwefelwasserstoffdruck, so findet Abscheidung eines festen Produkts statt, das an Schwefelwasserstoff reicher ist als die flüssige Phase. Wir haben mit verschiedenen chemisch-physikalischen Methoden festgestellt, dass das erste feste Produkt $HSCH_2$-$SCH_2SCH_2OCH_2OH$ ist. Weiters wird ein Mechanismus beschrieben, der die Bildung dieses Produkts aus der flüssigen Phase erklären kann.

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