B was finely cut and allowed to soak in benzene as long as soluble matter diffused out. This soluble material (2.8 g.) was added to fraction A-7 and was also refractioned. The results appear in Table II.

TABLE II

SECONDARY FRACTIONATIONS

Initial material	Fraction	Weight, g.	S, %	Solubility in C_6H_6	
A-1, A-2 and A-3	A_2-1	13.7	0.058	Sol.	$RS_1 = 0.0574\%$ S
	A_2-2	8.0	.057	Sol.	
	A_2-3	4.8	.056	Sol.	
	A_2-4	8.0	.043	Sol.	
A-4, A-5 and A-6	A_2-5	2.8	.115	Sol.	$RS_2 = 0.1153\%$ S
	A_2-6	3.9	.112	Sol.	
	A_2-7	8.1	.117	Sol.	
A-7 and part of B	A_2-8	4.0	.179		

C. Analytical Procedure

The finely cut rubber samples were extracted with acetone in a Soxhlet apparatus for twenty-four hours, swelled with benzene, soaked in alcohol and freed of inorganic sulfides.[4] Blank runs demonstrated that this treatment was adequate. The sulfur content[3] was determined by the procedure of Wolesensky. All results were corrected for parallel blank determinations.

Due to the limited amount of material available, double analyses were performed only in a few cases; with only one single exception the results checked within experimental error, and in the exceptional case, a third analysis secured the needed confirmation.

During the course of the fractionation it was noted that vulcanization was still progressing and also that traces of unreacted accelerator were removed by the solvents used in the fractionation. This explains why the total amount of combined sulfur was not constant after each fractionation. As the theoretical reasoning is based only on the final results, when the sulfur concentration no longer changed, it is not affected by these details.

Conclusion and Summary

Partially vulcanized rubber has been fractionated into components in which rubber is combined with increasing amounts of sulfur. The analyses of these fractions concur to indicate a molecular weight of about 54,000 for the particular sample of rubber used. Specimens of varied origin, can thus have their molecular weight measured by strictly orthodox chemical means.

THE MIDGLEY FOUNDATION
COLUMBUS, OHIO

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(4) Stevens, *Analyst*, **40**, 275–281 (1915).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XIV. A Structural Formula for Ebonite

BY THOMAS MIDGLEY, JR., ALBERT L. HENNE AND A. F. SHEPARD

The ninth paper of this series[1] reported a list of compounds obtained by the pyrolysis of ebonite and stated that their correlation might elucidate the constitution of ebonite.

The compounds positively identified, and their relative amounts, were benzene, <0.5; 2-methylthiophene, 10; toluene, 1; 2,3-dimethylthiophene, 50; 2,4-dimethylthiophene, 10; *m*-xylene, 50; 2-methyl-5-ethylthiophene, 240. Moreover, it was established definitely that thiophene itself, and those of its homologs with less than eight atoms of carbon other than the ones just mentioned, were positively absent.

The above compounds are obtained by themselves only when ebonite is destructively distilled. Mixtures of raw rubber and sulfur yield other isomeric forms as does the reaction of sulfur with the pyrolysis products of raw rubber. For example, ebonite yields only 2-methylthiophene, while isoprene and sulfur yield only 3-methylthiophene;[1] a mixture of raw rubber and sulfur yields both isomers. Hence the compounds actually isolated were derived from fragments of the ebonite molecule and not merely from fragments of the rubber molecule with sulfur subsequently attached.

The identified decomposition products accounted for only 1.1% of the original material and it is therefore possible that the type of sulfur linkage developed in the following reasoning is not the only one present.

I. Only four out of the twenty-one possible thiophenes of substantially equal stability with less than eight carbon atoms were produced. Random linking of small fragments after extreme

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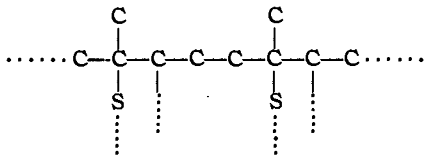
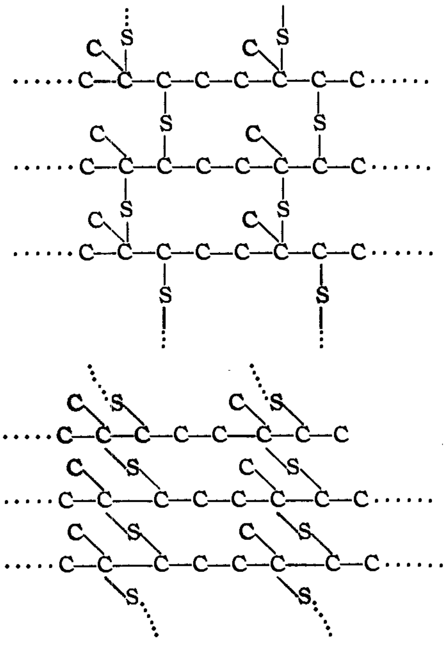
(1) THIS JOURNAL, **54**, 2953 (1932).

pyrolysis is unacceptable as an explanation of their origin, and consequently they are accepted as representing fragments of the parent molecule.

II. All four sulfur compounds bear a methyl group in the alpha position, showing that sulfur is linked to a tertiary carbon atom in ebonite, thus



III. The absence of thiophene itself, of 2,3-methylethylthiophene and of 2,5-dimethylthiophene demonstrates that sulfur did not link two distinct rubber molecules. There are three significant ways to make intermolecular linkages in accordance with the formula $(C_5H_8)S$, *i. e.*



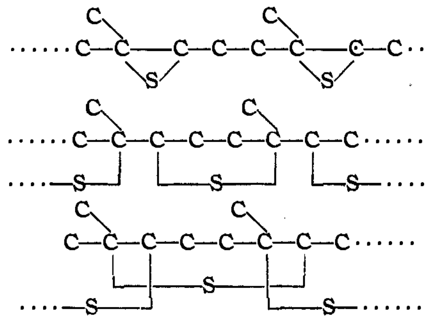
I

II

III

As a thiophene ring is not present in any of these formulas, the assumption would have to be made that it forms only during pyrolysis. I and II are eliminated because I would lead by such a process to the formation of thiophene itself, and some other homologs not found, while II would form 2,5-dimethylthiophene along with other isomers which were absent. It is considerably more difficult to reject III, as this type is able to form every one of the compounds actually found by pyrolysis, and only one which was absent, namely, 2-methyl-3-ethylthiophene. Even after disregarding this last objection, it is hard to see how III could prevail to the practical exclusion of I and II, without assuming the action of directive forces during the combination of the sulfur and the rubber. Since this does not seem justified it is necessary to abandon intermolecular linkages of sulfur from further consideration.

IV. The three preceding paragraphs narrow the possible simple formulas representing the original rubber molecule saturated with sulfur to



(1)

(2)

(3)

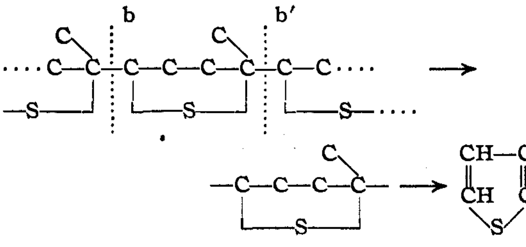
Since they bear no relationship to the decomposition products, (1) and (3) are immediately eliminated. On the other hand (2) correlates very nicely.

Discussion

The following paragraphs demonstrate the simplicity of the relationship existing between formula (2) and the products found, without claiming a representation of the *actual* pyrolysis steps.

The process is to consider groups from the parent molecule consisting of 5, 6, 7 and 8 carbon atoms and to observe the relationship between these groups and the corresponding products obtained. The carbon skeleton will be discussed exclusively, and the postulates of paper I[2] of this series regarding the behavior of hydrogen atoms and partial valencies will be adhered to.

If the ebonite molecule splits along the lines b and b′, the formation of α-methylthiophene is at once evident. A split along a and b′ gives 2-methyl-5-ethylthiophene. Since this compound predominates among the decomposition products, it seems that a rupture can occur along a and b′



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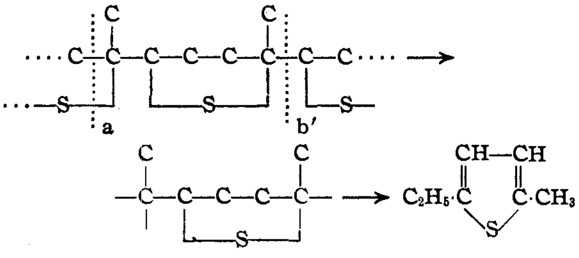
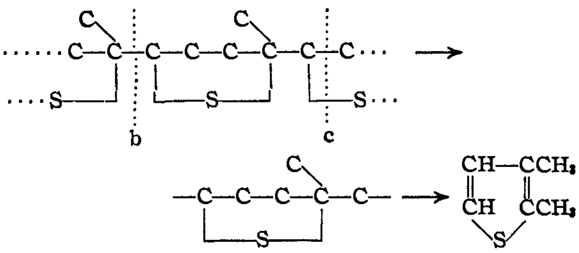
(2) Midgley and Henne, THIS JOURNAL, 51, 1222 (1929).

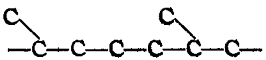
more easily than along b and b′. Hence a splits oftener than b.

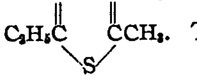
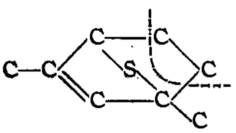


A split along b and c yields a fragment which can give only a hydrothiophene derivative. A methyl group must migrate if a thiophene derivative is to be obtained. In this way the formation of 2,3-dimethylthiophene is explained.



Although the rupture (b and c) may be as frequent as that of (b and a), the complexity of the rearrangement can be expected to minimize the formation of 2,3-dimethylthiophene. If the preceding premises on the relative strength of the bonds are correct, then splits along (a and c) should be the most frequent and form fragments represented by



Its rearrangement may lead to a thiophene homolog, by migration of one of the methyl groups to yield  This compound was outside the range of the investigation. Another possibility is that the terminal carbon atoms link to form a six side ring such as  from which the loss of hydrogen sulfide explains the formation of *m*-xylene and the loss of two carbons gives 2,4-dimethylthiophene.

The possibility of having the same fragment form three different compounds accounts for the low relative yield of each.

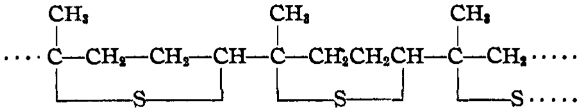
The remaining sulfurated compounds which were only partially identified could easily be derived from the proposed formula. It is thus concluded that the proposed type of sulfur linkage was preponderant, and may even have been the only one present.

It is admittedly pure speculation to project the above formula into three dimension space, yet the process carries with it some attractive possibilities. It has often been suggested that the rubber molecule is extensible and that it is a helix. If the sulfur atoms are linked in this helix as above described by the plane formula, it can be seen that the sulfur atoms tie together successive turns of the helix, and render it rigid. If sections are cut from this spacial formula, all the decomposition products found, and only those, are either obtained directly or by ring closure between carbon atoms adjacent in space.

A further consideration applies to soft cured rubber, where an occasional turn of the helix would be prevented from opening upon stretching by the linkage of a sulfur atom. "Nodules" would thus be created, which would so key the structure together that slippage between the molecules would be prevented, and tensile strength materially increased.

Summary

A formula for ebonite has been proposed, where sulfur is linked to a carbon atom bearing a methyl group on the one side and to the next third carbon atom of the rubber chain on the other side



$$\cdots\mathrm{C(CH_3)-CH_2-CH_2-CH-C(CH_3)-CH_2CH_2CH-C(CH_3)-CH_2}\cdots$$

This formula is based on a consideration of the pyrolysis products of ebonite.

COLUMBUS, OHIO RECEIVED NOVEMBER 15, 1933