expected if it is assumed that the impurities act as chain-transfer agents.

Only vinylacetylene appeared to cause cross linking in the polymer. This gave rise to large amounts of benzene-insoluble gel (48%) when present to the extent of 1.00% of the butadiene.

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Sulfur Linkage in Vulcanized Rubber

REACTION OF SULFUR WITH 2-METHYL-2-BUTENE[1]

MILTON L. SELKER[2] AND A. R. KEMP
Bell Telephone Laboratories, Murray Hill, N. J.

The reaction of 2-methyl-2-butene with sulfur at 111.6° C. was studied. Reaction time and concentration paralleled those common in rubber-sulfur vulcanization. The results offer further insight into the vulcanization problem. The products of the reaction are liquids of the polysulfide type R-S_x-R, where *x* varies from 2 to 6 and R is an alkyl or alkenyl group and two solids ($C_5H_6S_3$ and a higher homolog). The polysulfides appear to be somewhat richer in hydrogen than is expected from reaction of two C_5H_{10} molecules, whereas the solids are hydrogen-poor. The structure of an acid anhydride in the sulfur system showing thione-thiol tautomerism is proposed for $C_5H_6S_3$, which is therefore 2,5-dithione-3-methyltetrahydrothiophene. The color changes with reaction time, from yellow to red to black, parallel those of rubber-sulfur vulcanizates. As in rubber-sulfur vulcanization the sulfur reaction rate is directly proportional to time, although the absolute rate is twice that in the polymer system. Starting with equal mole quantities of olefin and sulfur, there is a considerable amount of unreacted olefin in the system when all of the sulfur has reacted. The shorter the reaction time, the higher the value of *x* in the polysulfide R-S_x-R and the larger the percentage of residues R that are saturated.

YEAR by year the complete definition of vulcanized rubber in terms of organic chemistry has become more desirable. The severity of the demands on rubber products makes it imperative to extend basic knowledge of vulcanization if we are to overcome the traditional defects or use limitations in this field.

Chemical investigations of the vulcanization problem can be arranged into three lines of attack. In the first method the vulcanizate network is severed at various points by chemical or thermal means to liberate small portions of the material which can be studied as are small molecules. Ideally there should be no alteration of the linkages except where cutting of the chains takes place. Unfortunately no such "scissors" are known. Midgley, Henne, and Sheppard (*15*) applied the thermal decomposition method to ebonite. Their study of the fragments, based on 1% of the total material involved, was inconclusive.

Secondly, a small molecule reagent which will swell the rubber may be used to penetrate the three-dimensional network and react with the various linkages in it. This method was used by Meyer and Hohenemser (*14*), who diffused methyl iodide into vulcanized rubber. This complicated reaction and its background with pure sulfur compounds was reported in the first two articles in the present series (*20*). The conclusions of this study were that the part of the combined sulfur which could be removed as trimethyl sulfonium iodide was sulfide sulfur linked to a carbon atom alpha to a double bond. In most cases the less of this type of sulfur present, the higher the tensile strength of the vulcanizate. Methyl iodide was successful to a hitherto unattained degree because both its rate of reaction and products vary with the type of sulfur bond. This work left unanswered the question of the sulfur linkages which were not attacked by methyl iodide—in some cases the greater part of the combined sulfur.

The third chemical line of attack is the study of model systems. A small molecule, such as an olefin, is reacted with sulfur and rubber-compounding ingredients; then, from identification of the products and study of the reaction, conclusions concerning vulcanizates are reached by analogy. The use of this method is old in chemical problems.

In 1916 Friedmann (*9*) first used the reaction of simple hydrocarbons with sulfur in an effort to find out more about the origin of the sulfur compounds in Mexican petroleum. It was not until 1935 that Schwarzkopf (*19*) proposed the use of model systems for the study of rubber vulcanization. His choice of ethyl cinnamate was somewhat unfortunate, as it is not a very close parallel to rubber stucture.

In 1944 Armstrong, Little, and Doak (*2*) published the results of a great deal of work on the reaction of sulfur alone and with compounding ingredients, on the olefins 2-methyl-2-butene, 2-methyl-1-butene, 2-butene, cyclohexene, and 5-methyl-4-nonene. They concluded that "sulfur vulcanization of rubber is due chiefly to the formation of disulfide and monosulfide cross links, which are attached to the α-methylene group or the α-methyl group of the rubber chain."

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[1] The first two papers in this series appeared in January 1944 (*20*).
[2] Present address, 13,400 Shaker Blvd., Cleveland 20, Ohio

Table I. Reaction of 2-Methyl-2-butene with Sulfur at 141.6° C.

Run	Orig. Sulfur, %	Time, Hr.	Sulfur Reacted, %[a]	Olefin Reacted, %	Reaction Mixture: Liquid color	Reaction Mixture: Solids
1[b]	7.00	1	19.2	3	Pale yellow	Sulfur needles
2	7.20	2	46.3	4	Light yellow	Sulfur needles
3	7.12	4	93.7	8	Light orange	Yellow-green rhombic sulfur
4	7.59	8	100	11	Orange-red	None
5	9.25	24	100	20	Dark red	0.7 $C_5H_6S_3$[c, d]
6	32.6	24	100	73	Black-red	1.47 $C_5H_6S_3$[c], yellow-brown
7	31.8	32	100	77	Black	3.22 $C_5H_6S_3$[c], brown-black

[a] Percentage of total sulfur that reacted.
[b] Inadequate shaking; reaction rate is somewhat low.
[c] Percentage of total sulfur-containing products.
[d] In solution.

REACTION OF 2-METHYL-2-BUTENE WITH SULFUR

The reaction of 2-methyl-2-butene and sulfur was carried out in glass pressure flasks. After proper time at low temperatures to encourage crystallization of sulfur and solid products, the bomb was opened, the unreacted olefin was stripped off under vacuum, and the sulfur products were put through a molecular still. As much product was removed as was possible at room temperature.

In order to ensure that very little of the sulfur itself would remain dissolved in the reaction mixture, the solubility of sulfur in 2-methyl-2-butene was investigated. It is 0.73 and 0.18% at 30° and 4° C., respectively. In allyl disulfide the solubility was 2.50 and 1.37% at 26° and 4° C., respectively. Thus some sulfur would be left in the reaction mixture even if it stood at 0° C. for some time. For this reason it is preferable to hold the reaction bulb at −78° C. for some days after the reaction before opening, to crystallize all the solid products. The reactants, conditions, and pertinent data for the seven runs made with 2-methyl-2-butene are given in Table I. Table II gives the detailed analysis of the products of each run.

Reaction times of over 4 hours do not give any solid residue of unreacted sulfur in the bomb. Run 4, for instance, has no solid in the cooled reaction vessel. In runs 2 and 3, where unreacted sulfur remained, the small amount of dissolved sulfur in the stripped reaction products came over in the molecular distillation. The crystals indicated in run 2, fractions 3 and 4, and in run 3, fractions 4 and 5 (Table II) are sulfur. They were isolated and identified by analysis.

However, in runs 6 and 7 a solid is again present in the cooled reaction bomb. This solid was yellow-brown in run 6 and brown-black in run 7. Examined under the microscope, the crystals of run 6 were yellow thick columns. The run 7 solids product was composed of two types of material, yellow needles and black spherulites. These materials are the hydrogen-poor products discussed below.

In runs 5 and 6 no attempt was made to crystallize these solid products in the unopened bond. Consequently the hydrogen-poor solid products of these runs were recovered as solids plus some liquid, on the condenser of the molecular still with the pot at room temperature (Table II, run 5, fraction C, and run 6, fraction 2S). This was possible only because the condenser temperature was −78° C. If tap water had been used instead, the solubility of the solid products in the liquid products was high enough so that no solid would have been detected in the condensate at all. In run 7 an effort was made to freeze out all the solid product by leaving the unopened bomb at −78° C. for 7 days. This was successful, and very little additional solid was obtained by molecular distillation of the reaction mixture. These solids are fairly insoluble in petroleum ether at −78° C., so that they could be detected in the liquid hydrogen-rich products by diluting these fractions with 3 volumes of cold petroleum ether, cooling to −78° C., and filtering off the precipitated solids.

In several runs the recovered unreacted olefin was carefully fractionated. Only traces of lower boiling hydrocarbons were found. Therefore no appreciable isomerization of the olefin takes place in these reactions.

The products of the reaction are liquids of polysulfide type $R\text{-}S_x\text{-}R$, where x varies from 2 to 6 and R is an alkyl or alkenyl group and solids, two of which, $C_5H_6S_3$ and $C_{10}H_{10}S_3$, have been isolated. The former group is referred to as the hydrogen-rich product and the latter, the hydrogen-poor.

HYDROGEN-RICH PRODUCTS

The carbon and hydrogen analyses in Table II show that, in general, the hydrogen content of the liquids of type formula $R\text{-}S_x\text{-}R'$ is somewhat higher than could be expected by reaction of two C_5H_{10} molecules. Whether this hydrogen excess is real only further careful work will decide. If it is real, hydrogen transfer is indicated; this theory is supported by the presence of the two hydrogen-poor solid compounds, $C_5H_6S_3$ and $C_{10}H_{10}S_3$. Also noteworthy is the fact that the highest polysulfides tend to have hydrogen contents H_{21}, whereas the lower ones tend to $H_{20.5}$. H_{22} would result from two saturated residues, whereas H_{20} results from one saturated and one unsaturated group.

The empirical formulas of the type $C_{10}H_{20.6}S_x$ and $C_{10}H_{21}S_x$ given in Table II suggest that these fractions could be mixtures of the compounds $C_{10}H_{18}S_x$, $C_{10}H_{20}S_x$, and $C_{10}H_{22}S_x$. The higher, initially formed polysulfides appear to have more saturated residues than do the lower polysulfides. The shorter the time of reaction, the higher the polysulfide formed. This is shown by consideration of Table II where, for the 2-hour reaction, 81% of the product is higher than $—S_{5.7}—$, for the 4-hour run 50% is above $—S_{5.5}—$, and for the 8-hour run no higher product than $—S_{4.5}—$ is isolated.

Fractions 1, 2, 3, and 6 of run 3 were reacted with methyl iodide according to the standard procedure (*20*). The results are shown in Table III. The methyl iodide reaction shows that the amount of dialkenyl polysulfide is greatest in the volatile fraction 1 with some in 2 but none in fractions 3 and 4. More iodine should be liberated, but it is probably taken up by the sulfur linkages and the carbon-carbon double bonds. Fractions 3 and 6, therefore, may contain alkyl alkenyl polysulfides and/or dialkyl polysulfides. The mercuric iodide–catalyzed reaction with methyl iodide confirms this by showing but few crystals of $(CH_3)_3\,SI\cdot HgI_2$, which results from dialkenyl sulfides, but much iodine and an oily layer; the latter probably contains products of the type dimethyl alkyl sulfonium iodide$\cdot HgI_2$, where the alkyl is an amyl group of some type. The terms alkenyl sulfide, etc., include only those unsaturated residues in which the sulfur linkage is alpha to the double bond.

HYDROGEN-POOR PRODUCTS

The hydrogen-poor products are found only in small quantities in the reaction mixture on long heating. Two compounds have been isolated: $C_5H_6S_3$, yellow needles, analysis given in Table II, run 6, fraction 2S; $C_{10}H_{10}S_3$ (?), brick-red needles, melting point 197° C., analysis 51.9% C, 4.69% H. Since only about 8 mg. of the higher melting compound were isolated, no extensive purification was possible, and the empirical formula given is tentative. Enough of the lower melting compound, $C_5H_6S_3$, was purified and available for carrying out various reactions.

A search of literature revealed one compound of the formula $C_5H_6S_3$. Barbaglia (*4*) in 1884 had prepared it from isovaleraldehyde.

This reaction was repeated. A yellow-orange crystalline compound (melting point, 95.0° C.) was isolated from the liquid reaction products. The $C_5H_6S_3$ from sulfur reaction with 2-methyl-2-butene had a melting point of 95.2° C. The mixed

TABLE II. ANALYSIS OF PRODUCTS

Run	Fraction	Bath. Temp., ° C.	Per Cent	Color	State (L = Liquid, C = Crystals)	C/H	H, %	C, %	S, %	Total, %	Mol. Wt.	n_D^{25}
1 (1 hr.)	1	40	42.2	Yellow	L	..	...	...	50.9	...	230	....
					Calcd. for $C_{10}H_{21}S_3$	..	...	...	50.6	...	237	....
	2	>40	57.8	Yellow-orange	L (viscous)	..	...	...	61.6	...	430	1.6638
2 (2 hr.)	1	23	1.3	Light yellow	L	..	...	...	51.1	...	..	1.5779
					Calcd. for $C_{10}H_{20.6}S_{4.6}$	..	...	...	51.2	...	288	....
	2	29	26.5	Yellow	L	5.80	6.4	36.8	56.3	99.5	228	1.6060
					Calcd. for $C_{10}H_{20.6}S_{5.7}$	5.79	6.4	37.2	56.4	...	323	....
	3	30	24.3 / 0.7	Yellow	L / C, sulfur	..	...	...	58.4	...	248	1.6187
					Calcd. for $C_{10}H_{20.6}S_{6.1}$	..	...	...	58.2	...	336	....
	4	33–140	31.7 / 4.6	Red-orange	L / C, sulfur	5.68	6.1	34.6	59.1	99.8	305	1.6355
					Calcd. for $C_{10}H_{21}S_{6.5}$	5.67	6.1	34.4	59.6	...	349	....
	Residue	>140	1.2	....	....	..	...	...	...	...	..	....
	Trap	....	2.3	....	....	..	...	...	...	...	..	....
	On condenser	....	3.5	....	....	..	...	...	...	...	..	....
	Loss	....	3.9	....	....	..	...	...	...	...	..	....
3 (4 hr.)	1	31	14.3	Yellow	L	5.95	6.89	40.95	47.5	95.4	180	1.5670
					Calcd. for $C_{10}H_{20}S_4$	5.96	7.44	44.6	47.5	...	269	....
	2	31	16.4	Yellow-gold	L	5.86	6.49	38.1	54.4	98.9	236	1.6001
					Calcd. for $C_{10}H_{20.3}S_{5.2}$	5.87	6.66	39.1	54.2	...	307	....
	3	31	13.6	Yellow-gold	L	5.76	6.50	37.45	55.4	99.4	225	1.6042
					Calcd. for $C_{10}H_{20.6}S_{5.5}$	5.78	6.54	37.85	55.6	...	317	....
	4	31– 80	7.01 / 0.38	Gold	L / C, sulfur	..	...	...	55.3 / 99.1	...	255	1.6160
	5	90	10.8 / 0.79	Gold	L / C, sulfur	..	...	...	54.8 / 99.1	...	319	1.6127
	6	140	23.1	Red	L	5.90	5.91	34.95	58.7	99.6	307	1.6308
					Calcd. for $C_{10}H_{20.2}S_{6.2}$	5.90	6.00	35.45	58.5	...	339	....
	Residue	>140	0.51	Black	L (viscous)	..	...	...	...	...	..	....
	Trap	....	6.2	Light yellow	L (light)	..	...	...	...	...	..	...
	Loss	....	6.9	....	....	..	...	...	...	...	..	....
4 (8 hr.)	1	30	3.1	Red	L	..	...	...	...	...	..	1.5595
	2	30	32.4	Yellow-gold	L	..	...	...	44.6	...	211	1.5649
					Calcd. for $C_{10}H_{21}S_{3.5}$	..	...	...	44.3	...	253	....
	3	31	18.4	Orange	L	..	...	...	51.1	...	245	1.5860
					Calcd. for $C_{10}H_{21}S_{4.5}$	..	...	...	50.5	...	285	....
	4	35– 90	7.2	Orange	L	..	...	...	50.5	...	270	1.5868
					Calcd. for $C_{10}H_{21}S_{4.5}$	..	...	...	50.5	...	285	....
	5	90–140	31.2	Red-Black	L	..	...	...	51.4	...	326	1.5977
					Calcd. for $C_{10}H_{21}S_{4.7}$	..	...	...	51.6	...	292	....
	Residue	....	0.9	Black	L (viscous)	..	...	...	...	...	..	....
	Trap	....	5.2	Colorless	L	..	...	...	0.95	...	..	....
	Loss	....	1.5	....	....	..	...	...	...	...	..	....
5 (24 hr.)	1	25	1.1	Light yellow	L	..	...	...	30.5	...	211	1.4966
					Calcd. for $C_{10}H_{20.5}S_2$	..	...	...	31.3	...	205	....
	2	25	23.4	Yellow	L	5.81	10.2	59.0	30.3	99.4	201	1.5252
					Calc. for $C_{10}H_{20.5}S_2$	5.81	10.1	58.6	31.3	...	205	....
	3	30	16.8	Orange	L/C	..	...	...	39.9	...	206	1.5398
					Calcd. for $C_{10}H_{20.5}S_{2.9}$	..	...	...	39.8	...	234	....
	4	30	5.2	Orange	L	..	...	...	44.0	...	220	1.5598
					Calcd. for $C_{10}H_{20.7}S_{3.5}$	..	...	...	44.3	...	253	....
	C	30	6.1 / 0.7	Orange / Yellow	L / C	..	...	...	59.1	...	..	....
					Calc. for $C_5H_6S_3$	..	...	...	59.2	...	..	....
		30– 82	9.2	Red	L	5.76	8.3	47.5	44.3	100.0	278	1.5665
					Calcd. for $C_{10}H_{20.7}S_{3.5}$	5.76	8.3	47.5	44.3	...	253	....
	6	82–140	20.0	Red-black	L/C	..	...	...	46.2	...	344	1.5805
					Calcd. for $C_{10}H_{20.7}S_{3.8}$	..	...	...	46.4	...	263	....
	Residue	....	1.0	Black	L (viscous)	..	...	...	...	...	..	....
	Trap	....	11.9	Colorless	L	..	...	...	1.16	...	..	1.3943
	Loss	....	4.6	....	....	..	...	...	...	...	..	....
6 (24 hr.)	1	25	3.3	Yellow-gold	L	..	...	...	29.9	...	190	1.5252
					Calcd. for $C_{10}H_{21}S_{1.9}$	..	...	...	30.1	...	202	....
	2	30	12.5	Gold-orange	L	5.67	9.8	55.3	34.9	99.9	207	1.5252
					Calcd. for $C_{10}H_{21}S_{2.36}$	5.68	9.8	55.4	34.8	...	217	....
	2S	30	21.2 / 1.1	Orange / Yellow	L / C >Crystal anal.	9.81	3.8	37.3	59.1	100.2	172	....
	Reaction residue		0.37	Brown-yellow	C calcd. for $C_5H_6S_3$	9.83	3.8	37.1	59.2	...	162	....
	3	69	4.4	Red	L	..	...	...	45.9	...	286	1.5736
					Calcd. for $C_{10}H_{21}S_{3.7}$	..	...	...	45.6	...	260	....
	4	76.5	15.7	Red	L/C	5.68	7.9	44.8	47.3	100.0	311	1.5798
					Calcd. for $C_{10}H_{21}S_4$	5.68	7.9	44.6	47.6	...	269	....
	5	122	11.8	Dark red	L/C	5.71	7.4	42.3	50.3	100.0	304	1.5941
					Calcd. for $C_{10}H_{21}S_{4.5}$	5.68	7.4	42.2	50.5	...	285	....
	6	140	6.2	Black	L	5.81	7.6	44.3	47.8	99.7	334	1.5928
					Calcd. for $C_{10}H_{20.5}S_4$	5.82	7.7	44.7	57.4	...	269	....
	Benzene soln. residue	>140	4.1	Black	L (viscous)	6.32	5.8	36.8	35.3	78.0	470	....
					Calcd. for $C_{10}H_{18.8}S_{3.5}O_{4.5}$	6.34	5.9	37.2	34.7	...	323	....
	Trap	....	3.4	Yellow	L (viscous)	..	...	...	51.8	...	416	1.6142
	Sample cutter	....	1.4	Yellow	L	..	...	...	46.1	...	..	1.5713
	Loss	....	15.0	....	....	..	...	...	...	...	..	....
7 (32 hr.)	1	30	11.7	Yellow	L	..	...	...	...	...	..	....
	2	30– 34	21.0	Orange	L	..	...	...	...	...	..	....
	3	34– 45	9.8	Orange-red	L/dissolved crystals $C_5H_6S_3$	..	...	...	...	...	..	....
	4	50– 90	15.5	Red	L/dissolved crystals $C_5H_6S_3$	..	...	...	...	...	..	....
	5	90–140	21.1	Dark red	L/dissolved crystals $C_{10}H_{11}S_3$	..	...	...	...	...	..	....
	Residue	>140	9.8	Black	....	..	...	...	...	...	..	....
	Trap		8.2	Light yellow	....	..	...	...	...	...	..	....
	Loss		2.9	....	....	..	...	...	...	...	..	....
	Reaction residue		3.22	Yellow & black	C, mostly $C_5H_6S_3$	..	...	...	...	...	..	....

TABLE III. REACTION OF RUN 3 POLYSULFIDES WITH METHYL IODIDE AT 24° C.

		CH$_3$I Reaction			CH$_3$I + HgI$_2$ Reaction		
Fraction	Formula	Time, Hr.	Crystals, (CH$_3$)$_3$SI	Moles I$_2$/mole compound	Crystals, (CH$_3$)$_3$SI·HgI$_2$	Moles I$_2$/mole compound	Oily product (red-brown)
1	$C_{10}H_{20}S_4$	24	Many	..	Many	..	Much
1	$C_{10}H_{20}S_4$	190	Many	0.07	Many	0.51	Thick deposit
2	$C_{10}H_{20.3}S_{5.2}$	24	Small	..	Some	..	Some
2	$C_{10}H_{20.3}S_{5.2}$	190	Some	0.04	Many	0.85	Much
3	$C_{10}H_{20.6}S_{5.5}$	24	None	..	Few	..	Little
3	$C_{10}H_{20.6}S_{5.5}$	190	Small	0.02	Fair	0.93	Fair amt.
6	$C_{10}H_{20.6}S_{6.2}$	24	None	..	Very few	..	Little
6	$C_{10}H_{20.2}S_{6.2}$	190	None	0.02	Some	1.14	Fair amt.

melting point was 95.1° C. Therefore the same compound, $C_5H_6S_3$, results from action of sulfur with isovaleraldehyde as with 2-methyl-2-butene. The sulfur linkage on the terminal carbon atom in the 4 position of the 2-methylbutane carbon skeleton, which is suggested by the preparation of $C_5H_6S_3$ from isovaleraldehyde, fits in with the structure supported by the evidence to follow.

REACTION OF SULFUR WITH ISOVALERALDEHYDE. 16 grams of sulfur with 32 grams of Eastman White Label isovaleraldehyde were sealed in vacuo in a Carius tube. Reaction at 240° C. for 10 hours gave a red-black liquid with some black crystalline residue. Distillation of liquid gave 4 cc. water-white liquid, boiling point 82° C.; 17 cc. yellow liquid, b.p. 169–175° C.; 20 cc. orange liquid, b.p. 175–185° C.; and 4 cc. black tar. The orange liquid gave yellow-orange crystals on cooling to −30° C. Recrystallization from ethanol at −30° C. gave yellow needles, m.p. 95.0° C.

REACTION WITH METHYL IODIDE. 30 mg. $C_5H_6S_3$ in 20 cc. 50% methyl iodide in ethanol turned red-brown in 40 minutes. No free iodine was present. On chilling to −78° C. a red-brown precipitate was obtained. The brick-colored compound (m.p., 150.5–151° C.) had 40.4% I, 31.28% S; calculated for $C_5H_6S_3 \cdot CH_3I$, 41.8% I, 31.98% S.

REACTION WITH METHYL IODIDE–MERCURIC IODIDE. 30 mg. $C_5H_6S_3$ in 20 cc. 50% methyl iodide–ethanol with 0.5 gram HgI_2 reacted in 4 minutes to give a white-yellow precipitate. After cooling to −20° C. this was filtered off. The yellow compound (m.p., 131.0–131.2° C.) had 50.6% I, 11.94% S; calculated for $C_5H_6S_3 \cdot CH_3I \cdot HgI_2$, 50.2% I, 12.65% S.

REACTION WITH MERCURIC IODIDE. 50 mg. $C_5H_6S_3$ in 5 cc. ethanol were added to 12 cc. ethanol saturated with 2% HgI_2. A yellow precipitate was obtained immediately. This was filtered, washed with alcohol, and dried. It melted sharply at 192.5° C. if put in the bath at 189° C. It decomposed on longer heating to a black tar. It had 40.4% I and 15.1% S; calculated for $C_5H_6S_3 \cdot HgI_2$, 41.2% I and 15.5% S.

REACTION WITH IODINE IN CARBON TETRACHLORIDE. 100 mg. $C_5H_6S_3$ in 8 cc. carbon tetrachloride were added to 0.314 gram iodine in carbon tetrachloride. Red-brown precipitate appeared in a few minutes. Recrystallization from carbon tetrachloride gives red-brown microscopic needles (m.p., 135.2–136° C.). Analysis, 69.1% I, 17.9% S; calculated for $C_5H_6S_3 \cdot 3I$, 70.1% I, 17.7% S.

REACTION WITH CHLORINE AND WATER. 400 mg. $C_5H_6S_3$ were suspended in 10 cc. of glacial acetic acid to which 3 cc. of water were added (*7*, *13*). Chlorine gas was passed through the suspension kept at 10° C. until the solid disappeared. If the chlorine is passed in slowly the solution turns yellow, orange, red, then black, then quickly fades to a light yellow, all in a few moments.

The ether extract of the reaction mixture on occasion gave square plates soluble in alcohol, insoluble in water, m.p. 76–82° C., 49.7% Cl. More often no crystals appeared here.

The product from the water-acid solution was odorless. The two fractions, ether-soluble and water-soluble, were combined, taken up in ether, and added to an ether solution of *p*-toluidine. A white precipitate immediately fell out. On recrystallization from ethanol-water it had a melting point of 221° C. (turned yellow at 214° C.), 8.03% N, 10.3% S, 54.0 % C, 6.45% H. Calculated for *p*-toluidine sulfate [$(CH_3C_6H_4NH_2)_2 \cdot H_2SO_4$], 8.9% N, 10.2% S, 53.8% C, 6.4% H.

REACTION WITH RANEY NICKEL. Hydrogenation using the adsorbed hydrogen in Raney nickel was attempted according to the method of Mozingo and co-workers (*16*, *21*). Appreciable sulfur was removed this way, as shown by analyses of the nickel catalyst. Unfortunately only a few milligrams of this material were forthcoming: consequently no further information could be obtained.

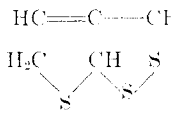
REACTION WITH COPPER OR SILVER POWDER. No desulfurization could be observed on refluxing copper or silver powder with $C_5H_6S_3$ in *n*-heptane.

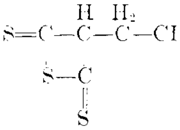
REACTION WITH GROTE'S REAGENT. Grote's reagent (*10*), a specially selective nitroprusside reagent for the mercaptan group, gave a positive red-purple test with $C_5H_6S_3$. This reagent was tested on several of the usual sulfur-containing rubber accelerators with the following result: Negative result (green coloration): 2-mercaptobenzothiazole, benzothiazyl disulfide, and piperidinium pentamethylene dithiocarbamate. Negative result (yellow coloration): trithiane, tetramethylthiuram disulfide, tetramethylthiuram monosulfide, *n*-propyl sulfide–*n*-propyl disulfide, and run 7, fraction 4 (a pentasulfide). Positive result (red-purple): thioglycolic acid (transitory), amyl mercaptan, and *tert*-amyl mercaptan. These last two gave a green color until reduced with potassium cyanide, whereupon they gave the usual red-purple.

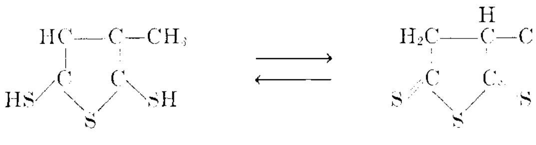
REACTION WITH ALKALI. Alcoholic potassium hydroxide added to $C_5H_6S_3$ in ethanol turned blue-red in 5 minutes. On addition of hydrochloric acid the color faded but was brought back by addition of alkali. Huppert (*12*) described a similar color change using the reaction product of sulfur and isophorone.

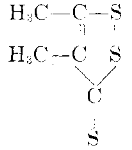
REACTION WITH SODIUM ETHYLATE AND POTASSIUM SULFIDE. On treating $C_5H_6S_3$ in ethanol with either sodium ethylate or potassium sulfide–potassium hydroxide solution (*8*), a red-blue water-soluble compound was formed that could not be separated from the salts present.

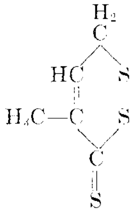
The empirical formula, $C_5H_6S_3$, and the molecular weight, 172, allow any of the following structures for this compound. These structures all have the 2-methyl-2-butene carbon skeleton, since it is unlikely that at 140° C. any carbon bonds would be broken and since no isomerization of the unreacted olefin takes place:


(*A*)


(*B*)


(*C*) (*D*)


(*E*)


(*F*)

After this article had been submitted for publication, the unpublished work of Bottcher and co-workers (*5*) in Germany became available. This series of three papers discussed in detail many compounds of the type $C_5H_6S_3$, which were named trithiones. The general structure *E*, where the methyl groups can be replaced by any hydrocarbon radical or hydrogen, was assigned on the basis of seven reactions. $C_5H_6S_3$ was prepared from isoprene and sulfur in 5% yield. According to Bottcher's own work, his structures *E* and *F* do not account for the addition of methyl iodide, which ordinarily splits a disulfide linkage. The oxidative splitting off of two sulfur atoms by hydrogen peroxide, which usually attacks C=S groups, is also not accounted for by either structure *E* or *F*. The structures *B* or *D* would satisfy these requirements.

The authors feel that the thione-thiol tautomerism displayed by compounds *C* and *D* accounts for most of the reactions observed. This structure was suggested for the colored compound 2,6-dithioketo-3,5-dimethyl-1-thio-4-pyranone by Schonberg and Asker (*18*). However, reaction of this compound with methyl iodide apparently does not follow the same course as does $C_5H_6S_3$.

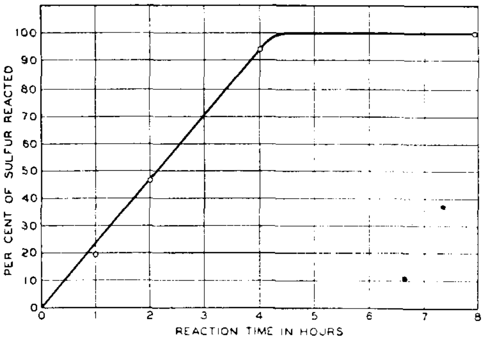


Figure 1. Effect of Time on Sulfur Reacted

Reaction of 2-methyl-2-butene with 7.4% sulfur at 141° C.

Structures *C* and *D* are felt to represent $C_5H_6S_3$ best for the following additional reasons: The methyl iodide reaction shows presence of a single sulfide sulfur not alpha to a double bond. This favors structures *B*, *C*, or *D*. The methyl iodide–mercuric iodide reaction shows the absence of disulfide or polysulfide sulfur. This again favors *B*, *C*, or *D*. Oxidation with chlorine removed all the sulfur. This would favor structures *B*, *C*, or *D*. Grote's reagent gives a positive test for mercaptan group. This would favor structures *C* and *D* over structure *B*, since the formation of a thiol structure from *B* leads to a sulfur bond on a carbon alpha to a double bond.

DATA SUMMARY

From the data given the following can be set forth concerning the reaction of 2-methyl-2-butene with sulfur at 141.6° C.:

The color changes with reaction time, yellow to orange to red to black, parallel those of rubber-sulfur stocks.

Sulfur combination rate is directly proportional to reaction time as in rubber-sulfur vulcanization (Figure 1).

The absolute reaction rate of 2-methyl-2-butene with sulfur is twice that of pale crepe rubber with sulfur.

Olefin combination rate is nearly proportional to time until the sulfur is completely combined, whereupon a further slow reaction takes place (Figure 2).

Starting with equal mole quantities of olefin and sulfur there is considerable unreacted olefin in the system when 100% of the sulfur has reacted.

Hydrogen transfer takes place resulting in what appear to be hydrogen-rich liquid products and small quantities of solid hydrogen-poor products.

The apparently hydrogen-rich compounds are polysulfides R-S_x-R′, where x varies from 2 to 6 and either R or R′ or both may be alkyl or alkenyl.

The hydrogen-poor compounds are solids, two of which, $C_5H_6S_3$ and $C_{10}H_{10}S_3$(?), have been isolated. A cyclic acid anhydride in the sulfur system with thione-thiol tautomerism has been proposed for the structure of $C_5H_6S_3$—that is, 2,5-dithione-3 methyltetrahydrothiophene.

Increased reaction time lowers the average value of x in the polysulfide products R-S_x-R′.

The higher the value of x in the polysulfide formula R-S_x-R′, the more hydrogen above the level H_{20} is present.

REACTION MECHANISM

The mechanism of the initial attack of sulfur in the form S_8 on the olefin is still unknown. In any case, the products which can be isolated from the short-term reaction are polysulfides, where the residues are saturated, unsaturated, or mixtures, but where the largest fraction is probably alkyl-alkenyl.

The hydrogen-poor compounds can result from the initial attack of sulfur on the olefin or from degradation reactions of the polysulfides on long-time heating.

There is another type of hydrogen-poor compound in the residue from molecular distillation. This is indicated by the higher carbon-hydrogen ratio of the residue in run 6 (Table II). Unfortunately the residues of other runs were not analyzed because of the small quantities involved and the difficulty of removing them from the molecular still. The removal involves the use of solvents and evaporation, which, as shown in the analysis, resulted in oxidation.

The viewpoint that studying model system 2-methyl-2-butene–sulfur will give results which can be applied to the rubber-sulfur system is strengthened by the linear nature of the reaction-time curve (Figure 1). In both cases the combination of sulfur varies directly with time. This similarity in kinetics certainly indicates that the mechanisms operating in the two cases are closely related.

The over-all reaction of methyl iodide on run 3 polysulfides (Table III) closely resembles that on the 100-rubber–8-sulfur stock SB1A described in a previous paper (*20*). At 24° C. half of the combined sulfur of this vulcanizate was removed. About the same per cent of the total sulfur-olefin reaction product gave large quantities of trimethylsulfonium iodide. The heavier polysulfides did not split out the latter compound, because at least one sulfur link was on a saturated hydrocarbon group. The sulfur that cannot be removed with methyl iodide at room temperature may be of two types: Either the sulfur is attached to saturated groups or it is in heterocyclic thiophenelike rings. The former will react when the temperature is raised, whereas the latter is stable to methyl iodide even at elevated temperature. On overcure the polysulfide sulfur reacts further both with double bonds and alpha carbon atoms. This is shown by the further slow reaction of the olefin after all the sulfur is combined (Figure 2).

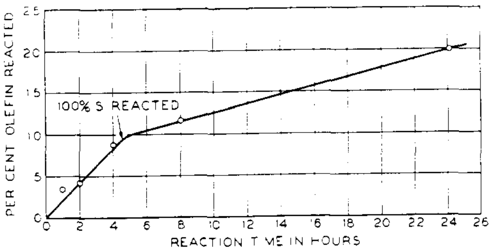


Figure 2. Effect of Time on Olefin Reacted

Reaction of 2-methyl-2-butene with 7.4% sulfur at 141° C.

There remains the reconciliation of the polysulfide formation observed in the 2-methyl-2-butene sulfur reactions with the generally accepted 32% combined sulfur limit in hard rubber.

EXPERIMENTAL DETAILS

2-METHYL-2-BUTENE. Cramer (*6*) disclosed a simplified way of preparing substantially pure olefin. He claims that by use of 48% sulfuric acid, *tert*-amyl alcohol can be selectively dehydrated in a mixture of other amyl alcohols to give a mixture of pure 2-methyl-1-butene and 2-methyl-2-butene. To check this, dehydration of practical *tert*-amyl alcohol was carried out using equal volumes of practical *tert*-amyl alcohol and 48% acid at 80° C. The olefins up to 40° C. were distilled off and fractionated in an eighty-plate column. Satisfactory 2-methyl-2-butene was produced in this way, although less 2-methyl-1-butene results than from use of pure *tert*-amyl alcohol. This method is much to be preferred, as it eliminates the tedious purification of *tert*-amyl alcohol. The 2-methyl-2-butene had a boiling point at 760 mm. of 38.5° C.; n^{25}_{D} 1.3843; freezing point, −133.6° C. These properties check those in the literature (*1*).

The purified olefin was collected during fractionation at −70° and stored at 0° C. in Pyrex bottles for 2 weeks in the dark. Then it was rebottled in 500-cc. Pyrex ampoules, which were frozen in liquid nitrogen, evacuated, and sealed. The glass-sealed evacuated ampoules of olefin were kept at room temperature in the dark until used. This storage period in some cases was 18 months.

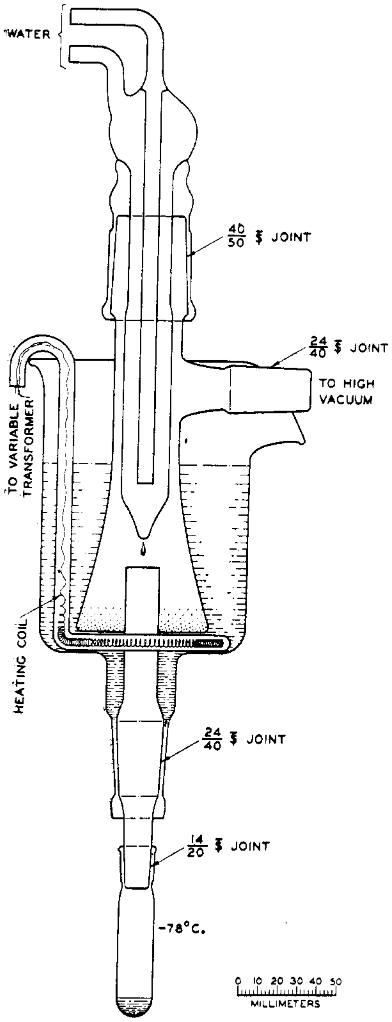


Figure 3. Improved Simple Molecular Still

Sulfur. This material, purified by the method of Bacon and Fanelli (*3*), was kindly supplied by Rocco Fanelli of The Texas Gulf Sulfur Company. The sulfur was powdered and stored in a desiccator over barium oxide.

Molecular Still. A small molecular still was constructed according to a design given by Riegel, Beiswanger, and Lanzl (*17*). This still was unsatisfactory for collecting small fractions.

The still of Hickman and Sanford (*11*) was modified so that fractions of a few drops could be collected and the heating bath precisely controlled. The final design shown in Figure 3 was quite satisfactory. The capacity is 40 cc.

Procedure. The glass reaction bulb was dried by evacuation for 1 hour and then filled with a weighed amount of sulfur and the contents of one 125-cc. ampoule of olefin added. The flask was then sealed off as described for pressure bulbs in the preceding article (*20*); this ensured removal of oxygen. The olefin weight was obtained by weighing the sealed bulb and sealed-off tip to 0.01 gram.

After weighing, the bulb was fastened in a special holder and placed in the heavy wire-mesh can. The can with the sealed bulb was placed in the shaker and immersed in the hot oil bath. The shaking rate was 4 cycles per second. A Micromax recorder-controller gave continuous temperature readings to ±0.2° C. The reaction time was taken from the moment of immersion to that of removal from the bath in analogy to rubber molding practice.

The bulb was allowed to cool to room temperature; it was then placed in the refrigerator at 0° C. for 48 hours. The bulb was then cooled to −78° C. for at least 1 day before it was opened at room temperature. The liquid product was decanted into a weighed, pear-shaped distilling flask. The solid in the bomb was washed quickly with petroleum ether at −20° C. and weighed. The petroleum ether wash was evaporated and the residue weighed and discarded if it was sulfur.

The liquid product was immediately stripped of its unreacted olefin by fractional distillation at a nitrogen pressure of 215 mm. of mercury; at this pressure 2-methyl-2-butene boils at 8° C. with a pot temperature of only 22° C. Any attempt to distill off the olefin at atmospheric pressure seriously changes the sulfur reaction products which turn black. The stripped sulfur-olefin liquid products were stored at 0° C. under nitrogen until they were molecularly distilled.

The molecular distillation was carried out at as low a temperature as possible and at as high a vacuum as the mercury diffusion pump produced. Here also any overheating resulted in change of the product color and character. The condenser was kept at −78° C. with dry ice and acetone. Fractions were taken on the basis of all the material which came over at a given temperature starting at 25° C. and slowly rising to 140° C. with pauses at 30°, 40°, 60°, 90°, and 140° C. The products were weighed and kept at 0° C. under nitrogen. In certain experiments solids were obtained on the condenser during the distillation. In this case the still was dismantled to remove the solid, reassembled, and the distillation resumed. The still was always cooled to room temperature before opening to air. When the solid reaction residue was not sulfur, it was sublimed in the molecular still. In this case the product was a solid adhering to the condenser.

Cryoscopic molecular weights were obtained using benzene. Melting points are the corrected values.

Refractive Index. The refractive index of the liquid products was determined in a Pulfrich refractometer. The index of the liquid polysulfides changed very rapidly on exposure to air, a change of 0.003 in 2 hours was common.

ACKNOWLEDGMENT

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