# A Contribution to the Chemistry of Rubber Vulcanization (Part I)

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## Diphenylmethane as a Model of Rubber Hydrocarbon and the Reaction of Dihenylmethane and Sulfur

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### Abstract

Diphenylmethane was used as a model of rubber hydrocarbon. Dibenzhydryl polysulfide, thiobenzophenone and hydrogen sulfide resulted from the reaction of diphenylmethane and sulfur at 180°C. Amount of hydrogen sulfide was equal to that of polysulfide plus thiobenzophenone. Dibenzhydryl disulfide and tetrasulfide were synthesized and decomposed. From analogy to autoxidation and from experimental results, it was deduced that dibenzhydryl polysulfide was the primary product, and thiobenzophenone was its decomposition product. The reaction mechanism was thoroughly discussed.

## 1. Introduction

After the discovery of vulcanization of rubber by C. Goodyear, a vast number of experiments and speculations have been carried out, but the final clarification of the mechanism of vulcanization and acceleration has remained unsettled. Overemphasis of physical and technological criteria in the investigation of vulcanization may have contributed to the failure to attach importance to the purely chemical investigation. In fact the rubber vulcanizates refuse chemical investigation, because they are insoluble and infusible.

However, in 1947 Farmer and collaborators[1], using olefinic substances such as cyclohexene, dihydromyrcene and squalene as model compounds, proposed a new theory on the vulcanization of rubber by sulfur. According to them $\alpha$–methylene adjacent to olefinic double bond is attacked by sulfur, and the hydrocarbon radical is formed. Then this radical couples with $\cdot S_x \cdot$ biradical, and the radical thus formed leads to polysulfide as a primary reaction products. Farmer's theory laid ground work for a chemical investigation of vulcanization, but the reaction of olefin with sulfur is too complex to decide the reaction mechanism.

Diphenylmethane (DPM) has a $\alpha$–methylene adjacent to double bond and may be expected to react with relative readiness. Moreover the reaction of DPM with molecular oxygene was already reported[2] to produce water, diphenylmethyl hydroperoxide, tetraphenylethane and benzophenone. It is expected that when DPM reacts with sulfur, the former gives the thioanalogs of above cited compounds. Since the reaction and reaction products of DPM with sulfur are considerd to be less complex than those of olefinic substances, the reaction mechanism will be elucidated by using the simpler hydrocarbon as a model compound. Comparative studies of the reaction with and without accelerator will present the key to the mechanism and theory of acceleration.

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As the fundamental studies of rubber vulcanization as well as acceleration the following two are the objects of this paper. The first is the reaction mechanism of DPM with sulfur at 180°C and the second is the pyrolysis of the primary product (dibenzhydryl polysulfide) to the secondary product (thiobenzophenone) at the same temperature.

Investigations on the reaction of DPM with sulfur in the presence of accelerator will be reported in other papers of this series.

## 2. Reaction of Diphenylmethane with Sulfur

### Experimental

Purified sulfur and diphenylmethane (DPM) which was redistilled directly before use, were heated in a flask equipped with condenser and innert gas inlet tube. The latter two were ground jointed to the reaction flask. Throughout the reaction time the innert gas (carbon dioxide or nitrogen gas) was passed gently into the flask, and the hydrogen sulfide evolveed was swept out from the flask through condenser and then absorbed in N/10–iodine solution. Iodine solution was titrated with thiosulfate after the reaction was completed. The reaction products other than $H_2S$ were distilled under diminished pressure (3 mm). Unreacted DPM distilled out at 95–105°C accompanied with thiobenzophenone (TBP) which had intense blue color. After TBP was converted to benzophenone by alcoholic potash, it was isolated from DPM and identified as 2,4–dinitrophenylhydrazone. The residues of distillation were sulfur and dibenzhydryl polysulfide (PS). PS which was freed from sulfur as well as possible by acetone, was digested in acetone solution with saturated aqueous sodium sulfite solution for a long time, and then converted to dibenzhydryl disulfide. After the acetone was distilled out, white needles crystal of disulfide was separated. m.p. 152°C and mixed m.p. with authentic sample 152°C. During the vacuum distillation of the reaction products of experiment No. 5, 6 and 7 in Table 1, the evolution of $H_2S$ was recognized. Absorbing tower filled with solid lead acetate was inserted between manometer and receiver of distillation apparatus. Lead sulfide formed was separated from unchanged acetate by hot water and weighed. $H_2S$ amounts caught by lead acetate were tabulated in parenthesis in Table 1, and the total sumes of $H_2S$ absorbed

Table 1.  The Reaction Products of DPM and sulfur at 180°C.

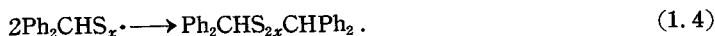| No. | DPM in m mole: S in milligram atom | Hour | Products in m mole | | |
|-----|-----|-----|-----|-----|-----|
|     |     |     | $H_2S$ | PS | TBP |
| 1 |           | 10 | 0.15 | trace | 0.05 |
| 2 | 200 : 400 | 20 | 0.60 | 0.1 | 0.44 |
| 3 |           | 30 | 1.14 | 0.21 | 0.87 |
| 4 |           | 50 | 1.55 | 0.48 | 1.05 |
| 5 |           | 10 | 0.66 (0.22) | 0.37 | 0.28 |
| 6 | 200 : 200 | 20 | 1.20 (0.14) | 0.81 | 0.30 |
| 7 |           | 30 | 1.45 (0.008) | 0.94 | 0.70 |
| 8 |           | 50 | 2.13 | 1.37 | 0.77 |

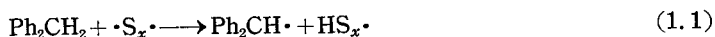In parenthesis, $H_2S$ caught by lead acetate.

by iodine solution and caught by acetate were showed in Table 1.

**Results and Discussions**

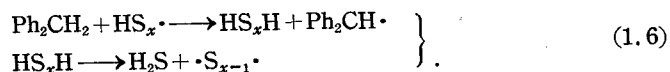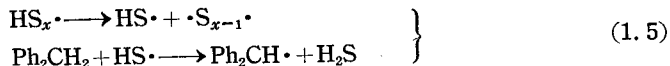The reaction products and their yields together with reaction conditions were summarized in Table 1.

From Table 1, the following important relation that the amount of $H_2S$ in m mole is nearly equal to the amount of PS plus TBP in m mole except for experiment No. 1 and 2, can be obtained. In experiment No. 1 and 2 the amount of the products (PS and TBP) was too small to obtain stoichiometric relation.

Experimental results lead to the mechanism which will be indicated as follows. DPM is dehydrogenated by sulfur biradical, producing diphenylmethyl radical and $HS_x\cdot$. This process is analogous to autoxidation and had been suggested already by Farmer[1]. Succeeding processes are eq. (2) and (3) or (4).

$$Ph_2CH_2 + \cdot S_x\cdot \longrightarrow Ph_2CH\cdot + HS_x\cdot \tag{1.1}$$

$$Ph_2CH\cdot + \cdot S_x\cdot \longrightarrow Ph_2CHS_x\cdot \tag{1.2}$$

$$Ph_2CH\cdot + Ph_2CHS_x\cdot \longrightarrow Ph_2CHS_xCHPh_2 \tag{1.3}$$

$$2Ph_2CHS_x\cdot \longrightarrow Ph_2CHS_{2x}CHPh_2\,. \tag{1.4}$$

Thus, dibenzhydryl polysulfide (PS) is considered to be the primary reaction poduct. It will be verified experimentally in next Section that PS decomposes to TBP at 180°C.

Hydrogen sulfide must result from $HS_x\cdot$. The reason for this is as follows. Experimental results showed that the reaction products at the higher sulfur dosage and at the shorter reaction time evolved considerable amount of $H_2S$ during vacuum distillation after reaction. This suggests that the hydrogen polysulfide ($H_2S_x$) may be formed and remain in the reaction products. Bacon and Farelli[3] confirmed that $H_2S$ was dissolved in molten sulfur and the solubility of $H_2S$ was the higher, the higher the temperature of molten sulfur. This indicates that $H_2S$ and sulfur form hydrogen polysulfide. In this paper, since $H_2S$ was swept out by innert gas, the inverse course of the case of Bacon and Fanelli is considered. Therefore, the mechanism of formation of $H_2S$ is either eq. (5) or eq. (6).

$$\left.\begin{array}{l} HS_x\cdot \longrightarrow HS\cdot + \cdot S_{x-1}\cdot \\ Ph_2CH_2 + HS\cdot \longrightarrow Ph_2CH\cdot + H_2S \end{array}\right\} \tag{1.5}$$

$$\left.\begin{array}{l} Ph_2CH_2 + HS_x\cdot \longrightarrow HS_xH + Ph_2CH\cdot \\ HS_xH \longrightarrow H_2S + \cdot S_{x-1}\cdot \end{array}\right\} \tag{1.6}$$

According to eq. (1.1), (1.2) and (1.3) or (1.1), (1.2) and (1.4), two of $HS_x\cdot$ are required to produce one of PS. On the other hand, according to eq. (1.5) or (1.6), two of $HS_x\cdot$ are equivalent to one of $H_2S$. Therefore, amount of PS in mole is equal to that of $H_2S$ in mole.

According to eq. (1.18) and (1.19) or to eq. (1.20), which will be cited and verified in the succeeding Section, in order to produce one of TBP from $Ph_2CHS_x\cdot$, one of $HS_x\cdot$ is required. Starting from DPM, two of $HS_x\cdot$ are required to produce one of TBP. Thus,

amount of TBP in mole is equal to that of H₂S in mole as well. The important result that amount of H₂S evolved is nearly equal to that of (PS+TBP) can be interpreted by the mechanism indicated above.

### 3. Pyrolysis of Dibenzhydryl Polysulfide

In preceding Section, radical Ph₂CHS$_x$· was assumed to decompose to TBP. In order to verify this assumption, in this Section dibenzhydryl disulfide (DS) as well as tetrasulfide (TS) was prepared and decomposed. In both cases the decomposition products were identified and estimated as far as possible.

**Experimental**

#### Preparation of dibenzhydryl sulfides

Disulfide : Thiobenzhydrol prepared from benzhydrol and thiourea hydrochloride, was extracted by benzene and oxidized to disulfide by iodone in alcohol.

$$C_{26}H_{22}S_2 : \text{ S\% calcd. 16.09 found 15.82}.$$
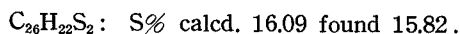
Tetrasulfide : Thiobenzhydrol distilled out at 98–99°C/0.03 mmHg. A 10% solution of sulfur chloride in carbon tetrachloride was added dropwise to a 10% solution of thiobenzhydrol in carbontetrachloride under nitrogen atmosphere. The mixture was cooled with ice and stirred for 4 hours. After the carbon tetrachloride was distilled out, ether was added. After standing, etherial solution gave crystalline tetrasulfide, which was recrystallized from petroleum ether.

$$C_{26}H_{22}S_4 : \text{ C\% calcd. 67.49 found 68.13}$$
$$\text{S\% calcd. 27.72 found 27.16}.$$
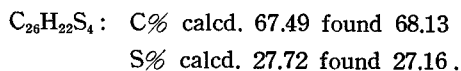
Dibenzhydryl tetrasulfide thus prepared is considered to have linear S–S structure,[4a] since sulfur chloride has linear ClSSCl structure.[4b] Monosulfide: As an authentic specimen, this compound was prepared from thiobenzhydrol and diphenylbromomethane.

#### Method of pyrolysis and estimation of products

Method of pyrolysis and determination of H₂S evolved were essentially the same as previous Section. The decomposition products were dissolved in alcohol. Undissolved portion A and alcoholic solution B were separated. B was diluted to 100 cc, and in a 5 cc aliquot TBP is determined by Kitamura's method.[5] To another 10 cc aliquot N/20–iodine solution was added. Excess iodine was titrated with N/20–thiosulfate. This iodine consumption was attributable to H₂S which remained in B, since B had no odor of thiobenzhydrol and precipitated lead sulfide with aqueous lead acetate solution. This showed that H₂S remained in B. The H₂S amount cited in Table 2 were the sum of that evolved during reaction and that remained in B. The succeeding procedures required to identify and estimate the products other than H₂S are summarized in Chart 1.

**Results and Discussion**

The decomposition products at 180°C for 2 hours were summarized in Table 2.
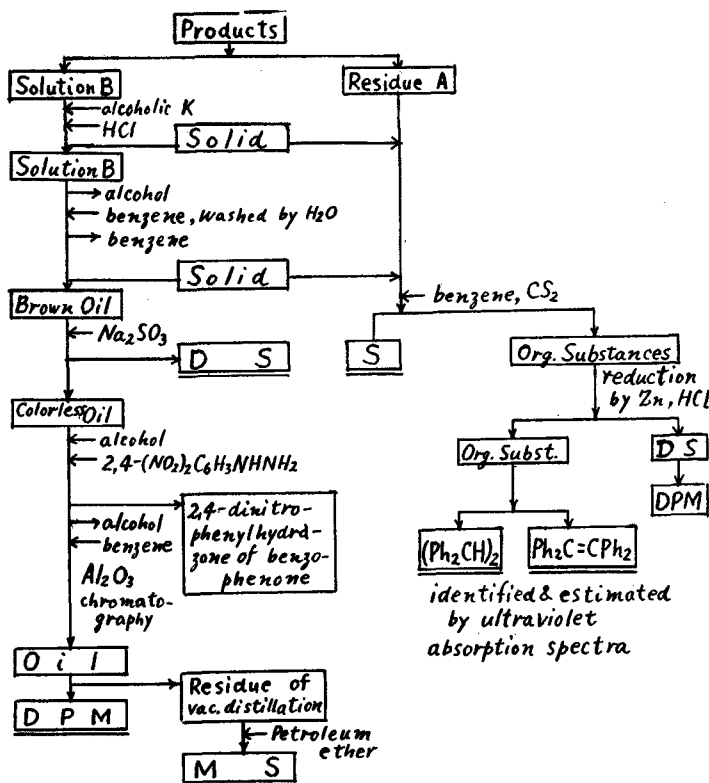
Chart 1. Procedures to identify and estimate the reaction products.

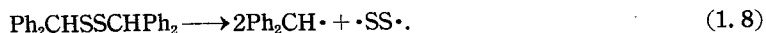Table 2. The Decomposition Products of DS and TS at 180°C for 2 hours.

| Starting Materials in m mole | Products in m mole | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | H$_2$S | TBP | Tetra-phenyl-ethane | Tetra-phenyl-ethylene | MS* | DS | PS | DPM | S |
| DS (12.5) | 0.53 | 3.63 | 3.02 | trace | 0.57 | — | 0.18 | 0.18 | 3.4 |
| DS (12.5) DPM (25) | 0.52 | 4.70 | 3.11 | trace | 0 | — | 1.20 | — | 1.25 |
| DS (12.5) S (50) | 0.54· | 9.49 | 0 | 0 | 0 | — | 1.38 | 0.53 | — |
| TS (12.5) | 0.90 | 12.72 | 0.07 | trace | 0 | 3.26 | — | 1.42 | 4.36 |

\* dibenzhydryl monosulfide.

It is well known[6] that disulfide decomposes into mercaptyl radicals as indicated in eq. (1.7).

$$Ph_2CHSSCHPh_2 \longrightarrow 2Ph_2CHS\cdot. \tag{1.7}$$

However, experimental results showed that the disulfide or tetrasulfide gave some free sulfur on pyrolysis. Therefore, C–S bond fission must occur in addition to S–S bond fission.

$$Ph_2CHSSCHPh_2 \longrightarrow 2Ph_2CH\cdot + \cdot SS\cdot. \tag{1.8}$$

In the case of tetrasulfide, the first step is considered as eq. (1.9) or (1.10).

$$Ph_2CHSSSSCHPh_2 \longrightarrow 2Ph_2CHS\cdot + \cdot SS\cdot \tag{1.9}$$

or
$$Ph_2CHSSSSCHPh_2 \longrightarrow 2Ph_2CH\cdot + \cdot S_4\cdot \quad or \quad 2\cdot S_2\cdot . \tag{1.10}$$
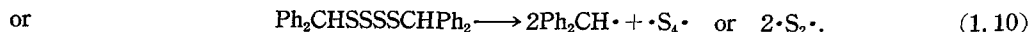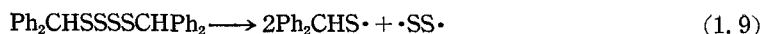
In the reaction mass of pyrolysis of DS or TS, the radicals $Ph_2CHS\cdot$, $Ph_2CH\cdot$ and $\cdot S_x\cdot$ are present. The formation of various decomposition products cited in Table 2 may be interpreted by the interaction of these radicals. Hydrogen abstraction is indicated in eq. (1.11).

$$Ph_2CHS\cdot + R\cdot \longrightarrow Ph_2C = S + RH \tag{1.11}$$

In eq. (1.11), $R\cdot$ represents $Ph_2CH\cdot$ or $\cdot S_x\cdot$. Therefore, RH is $Ph_2CH_2$ or $HS_x\cdot$. Radical $HS_x\cdot$ acts as $R\cdot$ again, and forms $HS_xH$. Hydrogen sulfide is formed from $HS_x$ or $HS_xH$.

Recombination is indicated in the following equations.

$$2Ph_2CH\cdot \longrightarrow Ph_2CHCHPh_2 \tag{1.12}$$

$$Ph_2CHS\cdot + Ph_2CH\cdot \longrightarrow Ph_2CHSCHPh_2 \tag{1.13}$$

$$Ph_2CH\cdot + \cdot S_x\cdot \longrightarrow Ph_2CHS_x\cdot \tag{1.2}$$

$$Ph_2CHS\cdot + \cdot S_x\cdot \longrightarrow Ph_2CHS_{x+1}\cdot \tag{1.14}$$

Polysulfide is formed by mutual recombination of $Ph_2CHS_x\cdot$ or recombination of $Ph_2CHS_x\cdot$ and $Ph_2CH\cdot$ as indicated by eq. (1.3) or (1.4) cited before. In the pyrolysis of TS considerable amount of DS was found as indicated in Table 2. This DS results from recombination of radical $Ph_2CHS\cdot$ produced in eq. (1.9). The formation of tetraphenylethane is prevented in the presence of enough amount of free sulfur as indicated by eq. (1.2). Dibenzhydryl monosulfide can not be produced in the presence of enough amount of free sulfur.

The mechanism of formation of trace of tetraphenylethylene is illustrated by following experiment. TBP, which was prepared by passing $H_2S$ and hydrogen chloride into an alcoholic solution of benzophenone under cooling and recrystallized from petroleum ether and dried in vacuum, was decomposed in the stream of nitrogen gas. The decomposition products are summarized in Table 3. The purity of thiobenzophenone thus prepared was determined by Kitamura's[5] method and was found to be 81%. Considering the preparation method, the remainder might be benzophenone.
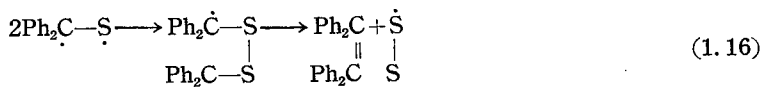
Table 3. The Decomposition Products of TBP at 180°C for 10 hours.

| Starting Materials in m mole | unde-composed TBP in m mole | Products in m mole | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_2S$ | tetra-phenyl-ethane | tetra-phenyl-ethylene | DS | S | PS |
| TBP (10) | 0.27 | 0 | 0 | 3.92 | 0 | 7.69 | 0 |
| TBP (10) DPM (191) | 3.63 | 0.10 | trace | trace | 0.40 | 0 | 0.12 |

From Table 3, it is concluded that in the pyrolysis of TBP alone it decomposes to 1 mole of tetraphenylethylene and 2 gram atom of sulfur. It has been already recognized by other investigators[8] that TBP is excited to triplet state. The facts that it can be readily autoxidized[7,9] and that it has intense blue color, support this. Therefore, the first step of decomposition of TBP is its excitation to triplet state.

$$Ph_2C = S \longrightarrow Ph_2C\text{—}\overset{.}{S} \tag{1.15}$$

and then

$$2Ph_2\underset{.}{C}\text{—}\overset{.}{S} \longrightarrow \underset{\underset{Ph_2\underset{.}{C}\text{—}S}{|}}{Ph_2\overset{.}{C}\text{—}S} \longrightarrow \underset{\underset{Ph_2C}{\|}}{Ph_2C} + \underset{\underset{\overset{.}{S}}{|}}{\overset{.}{S}} \tag{1.16}$$

The results in Table 3 indicate that in the presence of excess DPM eq. (16) is substituted by following eq. (1.17).

$$Ph_2\underset{.}{C}\text{—}\overset{.}{S} + Ph_2CH_2 \longrightarrow Ph_2CH\text{—}S\cdot + Ph_2CH\cdot. \tag{1.17}$$
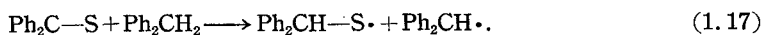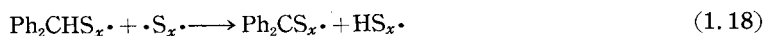
Table 2 also indicates that in the presence of DPM the amount of tetraphenylethylene approaches to zero at 180°C. In the reaction mass of DPM and sulfur at 180°C, excess of DPM and sulfur is always present. The formation of tetraphenylethane is suppressed by sulfur radical by eq. (1.2). Therefore, in the reaction product of DPM and sulfur at 180°C, both tetraphenylethane and tetraphenylethylene can not be found. In the reaction of DPM and sulfur, the primary product is PS. Radical $Ph_2CHS_x\cdot$ decomposed to TBP as indicated in eq. (1.11). Eq. (1.11) may be modified to (1.18) and (1.19).

$$Ph_2CHS_x\cdot + \cdot S_x\cdot \longrightarrow Ph_2CS_x\cdot + HS_x\cdot \tag{1.18}$$

$$Ph_2CS_x\cdot \longrightarrow Ph_2C = S + \cdot S_{x-1}\cdot. \tag{1.19}$$

If $\cdot S_x\cdot$ does not take part in the decomposition of $Ph_2CHS_x\cdot$ to TBP, the following eq. (1.20) is obtained by adding eq. (1.18) and (1.19).

$$Ph_2CHS_x\cdot \longrightarrow Ph_2C = S + HS_{x-1}\cdot. \tag{1.20}$$
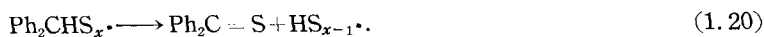
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4b) K. J. Palmer: J. Am. Chem. Soc., 60, 2360 (1938).
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   M. S. Kharasch, W. Nudenberg and T. H. Meltzer: J. Org. Chem. 18, 1233 (1953).
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9) A. Schönberg, O. Schütz and S. Nickel: Ber. 61, 2175 (1928).