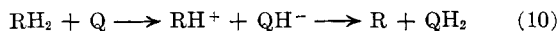The dehydrogenation reaction of hydroaromatic hydrocarbons by quinone was reported to proceed by the polar mechanism as

$$RH_2 + Q \longrightarrow RH^+ + QH^- \longrightarrow R + QH_2 \qquad (10)$$

where RH_2 and R represent dihydroaromatic and aromatic hydrocarbons, respectively, and Q and QH_2 quinone and hydroquinone, respectively.[14]

On the other hand, inhibition of free radical polymerization by quinone is well known and interpreted by a free radical mechanism,[15] although the actual mecha-

(14) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548, 3564 (1954); E. A. Braude, A. G. Brook, and R. P. Linstead, *ibid.*, 3569 (1954).

(15) C. Walling, "Free Radicals in Solution." John Wiley and Sons, Inc., New York, N. Y., 1957, p. 166.

nism is complex and obscure. The reaction of some hydrogen-donating compounds with quinone was reported to proceed by a radical mechanism,[16] the proof for which is initiation by sunlight and formation of coupling products, for example

$$2(C_6H_5)_2CH_2 + 2Q \longrightarrow (C_6H_5)_2CH\text{-}CH(C_6H_5)_2 + 2QH$$

where $2QH$ represents quinhydrone. In the present study it is difficult to decide whether the reaction proceeds by a free radical or polar mechanism, because of the high rate of the reaction. A comparative reaction of the corresponding thiol with benzoquinone indicates a far slower change to red. The red color suggests the addition of thiol to the quinone.

(16) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67 (1944).

Aralkyl Hydrodisulfides. II. The Thermal Decomposition of Benzhydryl Hydrodisulfide

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Decomposition of benzhydryl hydrodisulfide (RSSH) at 120° in the dark gave hydrogen sulfide, diphenylmethanethiol (RSH), and dibenzhydryl tetrasulfide (R$_2$S$_4$), and indicated a stoichiometric relation between the products and the starting material. The kinetics of decomposition of RSSH in biphenyl showed that formation of hydrogen sulfide and decomposition of RSSH are at an identical first-order rate. Light was found to increase the rate. Temperature dependence of rate of hydrogen sulfide formation in a temperature range from 100° to 150° gave the equation, rate of RSSH decomposition = $1.01 \times 10^6 \exp(-20.0 \text{ Kcal.}/RT)$. A simple, consecutive, free radical mechanism was proposed in which homolytic dissociation of the S—S bond of RSSH was concluded to be the slowest step. The mechanism of decomposition of the hydrodisulfide was compared with that of hydroperoxide or disulfide.

In the previous paper[1] of this series two aralkyl hydrodisulfides, benzyl and benzhydryl compounds, were allowed to react with 2,2-diphenyl-1-picrylhydrazyl or benzoquinone. The characteristic features of the reaction as compared with those of thiol and of other hydrogen-donating compounds were the high rate of dehydrogenation of the aralkyl hydrodisulfide by diphenylpicrylhydrazyl or benzoquinone and the formation of the diaralkyl tetrasulfide. It appears interesting to examine whether hydrodisulfide, the thio analog of hydroperoxide, behaves like the hydroperoxides, although an organic disulfide, the thio analog of a peroxide, is known to be much more stable than a peroxide. Among the alkyl and aralkyl hydrodisulfides so far prepared benzhydryl hydrodisulfide could be obtained in the crystalline state[2] and was chosen here as a representative of the hydrodisulfides.

Since hydroperoxides are known to decompose homolytically with heat or light,[3] the thermal decomposition of benzhydryl hydrodisulfide is examined in the present paper. The determination of the decomposition products in the absence of solvent as well as kinetic studies is reported and compared with that of hydroperoxides or dibenzhydryl disulfide. The analytical methods utilized here are specific and therefore will be described in detail.

(1) T. Nakabayashi and J. Tsurugi, *J. Org. Chem.* **28**, 811 (1963).

(2) J. Tsurugi and T. Nakabayashi, *ibid.*, **24**, 807 (1959).

(3) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York, N. Y., 1954, p. 88.

Experimental

Materials.—Benzhydryl hydrodisulfide was prepared by the method reported,[2] and recrystallized two times from petroleum ether (b.p. 40–60°) directly before use. This compound (m.p. 32.5–34°) was titrated by an ethanolic iodine solution,[2] and a purity of 99.5% was sufficient to obtain reproducible results. All the solvents used here were purified or dried from commercial products by conventional procedures.

Total Decomposition of Benzhydryl Hydrodisulfide.—A given amount (1.1618 g., 5 mmoles) of the hydrodisulfide was placed in a two-necked quartz flask with a condenser and a gas inlet tube, each of which had stop cock. Air in the flask was replaced with nitrogen by using three cycles of evacuation through the condenser and nitrogen streaming through the inlet tube. The flask, condenser, and inlet tube were wrapped with aluminum foil to be protected from light. Then the flask was heated at a given temperature.

(1) A gentle stream of nitrogen was passed through the inlet tube into the flask and then bubbled through the condenser into a series of three absorbing bottles, two of which contained an aqueous 0.1 N iodine solution and one of which an aqueous potassium iodide solution. The hydrogen sulfide evolved was swept by the nitrogen stream and absorbed in the bottles. Titration of an excess of iodine with sodium thiosulfate gave the amount of hydrogen sulfide evolved.

(2) After the reaction was completed, the contents of the flask were dissolved in benzene and the flask filled to 100 ml. An aliquot (20 ml.) of the solution after addition of ethanol was titrated with an aqueous iodine solution. The titration method with iodine which will appear below was always carried out by adding an excess of iodine and, if necessary, the solution allowed to stand for several hours and then the excess of iodine titrated with a sodium thiosulfate solution. After several washings with water and evaporation of the solvents, this aliquot gave a mixture of a viscous yellow oil and a crystalline benzhydryl disulfide. The latter was recrystallized from a solvent mixture of benzene–
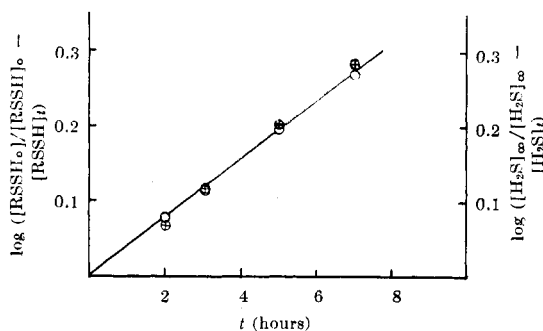
Fig. 1.—First-order plots for RSSH decomposition (—O—O—) and hydrogen sulfide formation (—⊕—⊕—) at 140° in biphenyl. Concentration, 0.5 mole/l.

ethanol (1:1), m.p. 152°, mixed melting point with an authentic sample,[2] 152°. Thus diphenylmethanethiol was identified by formation of the disulfide and estimated by titration.
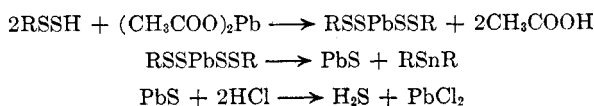
Desulfuration with Sodium Sulfite.—Farmer and Shipley[4] reported that some sulfur atoms involved in the polysulfides were removed by sodium sulfite, and that the polysulfide was reduced to disulfide in general. Titration of the sodium thiosulfate formed from the sulfite gave the amount of sulfur removed. In the present paper this method was modified as follows.

(3) Another aliquot (10 ml.) of the benzene solution was titrated, washed and the solvent evaporated as described in (2). The mixture of the oil and benzhydryl disulfide was dissolved in dioxane. To this solution was added 1 g. of sodium sulfite in 30 ml. of water. The mixture was refluxed gently for 3 hr., during which time nitrogen was slowly bubbled. After the organic layer was extraced with chloroform, the aqueous phase was cooled to 0°. To the solution was added 30 ml. of a 37% formaldehyde solution to combine with the excess sodium sulfite and then 20 ml. of glacial acetic acid. Titration with iodine gave the yield of sodium thiosulfate and hence the amount of sulfur removed.

(4) To determine the total yield of benzhydryl disulfide formed from the oxidation of the thiol and from the desulfuration of the polysulfides, the remaining portion (70 ml.) of the benzene solution was treated as described in (3), and the organic substances were extracted with chloroform. The extract was poured into 3000 ml. of water. Crystals were filtered and weighed.

Procedure for Kinetic Study.—The reaction was carried out in the same equipment and under the same atmosphere as for the total decomposition. To examine the effect of light, the flask was irradiated by a TOSHIBA SHL 100 ultraviolet mercury lamp (ν, 2540 Å.) at a constant distance of 50 cm. Otherwise, the reaction was conducted in the dark. The hydrogen sulfide evolved was measured at given time intervals by the same procedure as described in (1). Repeated additions of the measured amounts were plotted against reaction times. To determine the amount of unchanged hydrodisulfide, it is necessary to find an analytical method to determine this compound in the presence of the thiol and the polysulfides.

Analytical Method for Benzhydryl Hydrosulfide and Diphenylmethanethiol in a Mixture of the Hydrodisulfide, Thiol, and Polysulfide.—The thiol can be titrated by iodine or cupric oleate,[5] and gives 97.5 and 97.4% of the calculated values, respectively. The hydrodisulfide alone can be titrated by iodine and gives 99.5% of the calculated value, but can not be titrated by cupric oleate. The thiol alone, when treated by lead acetate and then hydrochloric acid, as described below in (5), gives 97.1% of the calculated value by the cupric oleate method. This indicates the reversibility of the thiol. On the other hand, 1 mole of the hydrodisulfide after the same treatment gives 0.5 mole of hydrogen sulfide and not the thiol. Benzhydryl hydrodisulfide was also found to give dibenzhydryl disulfide besides a viscous yellow oil after treatment with lead acetate, and after the lead sulfide formed was filtered and the filtrate passed through a silica column. The assumed reaction sequence is:

$$2RSSH + (CH_3COO)_2Pb \longrightarrow RSSPbSSR + 2CH_3COOH$$

$$RSSPbSSR \longrightarrow PbS + RSnR$$

$$PbS + 2HCl \longrightarrow H_2S + PbCl_2$$

(4) E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1531 (1947).

(5) G. R. Bond, Jr., *Ind. Eng. Chem., Anal. Ed.*, **5**, 257 (1933).

None of the analytical methods described above were found to be interfered with by the presence of dibenzhydryl tetrasulfide. Analysis for the thiol in the presence of the hydrodisulfide and the tetrasulfide gives the same value as for the thiol alone. Based on the results obtained, the following procedure was adopted.

(5) **Determination A.**—For a kinetic determination of the hydrodisulfide, the reaction was interrupted at a given time. The contents of the flask were dissolved in benzene and the flask filled to 50 ml. To an aliquot (10 ml.) of the solution was added 60 ml. of ethanol, and then an aqueous 0.05 N iodine solution. Titration of an excess of iodine with sodium thiosulfate gave the sum of the hydrodisulfide and thiol.

Determination B.—To another aliquot (10 ml.) of the benzene solution was added 40 ml. of benzene. The solution was shaken with an aqueous 20% lead acetate solution. The water layer was separated and the lead sulfide was filtered. The three cycles of shaking, separation and filtration were repeated. After several washings with water, the color of the benzene solution turned yellow, indicating the formation of lead thiolate. To the solution was added aqueous 6 N hydrochloric acid. The solution was washed with water, aqueous sodium bicarbonate solution, and again with water and dried with anhydrous sodium sulfate, filtered, and titrated with cupric oleate. This titration gave the amount of the thiol.

The value $(A - B)$ corresponds to the amount of the hydrodisulfide.

Results

All the decomposition experiments of the hydrodisulfide were carried out in the dark, unless otherwise described. Total decomposition of 5 mmoles of benzhydryl hydrodisulfide in an atmosphere of nitrogen for fifty hours at 120° gave 1.77 mmoles of hydrogen sulfide, 1.44 mmoles of diphenylmethanethiol, and 2.4 mmoles of dibenzhydryl disulfide, of which the latter was derived from oxidation of the thiol and from desulfuration of the polysulfide as well. The completion of the decomposition was ascertained by no further evolution of hydrogen sulfide. The yield of the polysulfides amounted to 1.68 (= 2.4 − 1.44/2) mmoles. Desulfuration of a mixture of polysulfides indicated that the amount of sulfur atoms removed from the polysulfides higher than disulfide was found to be 3.48 mg.-atoms. Hence, a mean value of x in polysulfide $[(C_6H_5)_2CH]_2$-S_{x+2} was approximately 2 ($\simeq 3.48/1.68$). This indicates that 1.68 mmoles of dibenzhydryl tetrasulfide were produced as a mean value.

The stoichiometric relations before and after decomposition are obtained from the analytical data of the products. The balance of hydrogen atom, benzhydryl group and sulfur atom are indicated in Table I, where figures in parentheses represent the amounts of the products in mmoles, and the integers numbers of atoms or groups involved in the products.

TABLE I

MATERIAL BALANCE AFTER TOTAL DECOMPOSITION OF 5 MMOLES OF RSSH

	H_2S	RSH	RS_4R	Total value in products	Starting value
H	(1.77) × 2	(1.44) × 1	—	4.98	5
R	—	(1.44) × 1	(1.68) × 2	4.80	5
S	(1.77) × 1	(1.44) × 1	(1.68) × 4	9.93	10

Table I indicates that other products than those cited above are not produced at all, or if produced, at a negligible amount.

The kinetics for decomposition of benzhydryl hydrodisulfide and for formation of hydrogen sulfide and of

TABLE II
DECOMPOSITION OF 5 MMOLES OF RSSH IN BIPHENYL AT 140°
(RSSH concentration, 0.5 mole/l.)

Time, hours	H_2S, mmole	RSH, mmole	Unchanged RSSH, mmole
2	0.24	0.28	4.20
3	0.41	0.29	3.90
5	0.64	0.48	3.15
7	0.82	0.54	2.72

diphenylmethanethiol at 140° in biphenyl is indicated in Table II.

The values of log ($[RSSH]_0/[RSSH]_0 - [RSSH]_t$) and log($[H_2S]_\infty/[H_2S]_\infty - [H_2S]_t$) plotted against reaction times are indicated in Fig. 1, where $[RSSH]_0$, $[RSSH]_t$, $[H_2S]_\infty$ and $[H_2S]_t$ represent initial concentration and concentration at time t of the hydrodisulfide and hydrogen sulfide concentrations after the total decomposition and at time t, respectively. Fig. 1 clearly indicates first-order rates of the hydrodisulfide decomposition and of hydrogen sulfide evolution and also indicates an identical value for both rates. Hereafter, the latter rate alone will be determined. The effect of light on the decomposition rate and the temperature dependence of the rate were studied in the absence of solvent and indicated in Fig. 2 and Fig. 3. When the two rates at the same temperature are compared with each other, the effect of light is observed in the runs where the decomposition is carried out under 120°. The effect of initial concentration of the hydrodisulfide in biphenyl on the rate was studied at 140° and tabulated in Table III.

TABLE III
RATES OF DECOMPOSITION OF RSSH AT 140° AT VARIOUS INITIAL CONCENTRATIONS

$[RSSH]_0$ in mmole	0.125	0.25	0.50	0.75
k (sec^{-1} 10^5)	2.175	2.24	2.29	2.38

The gradual increase of the rate is observed in passing from dilute to concentrated solutions. However, the approximate constancy of the k values for various initial concentrations indicates that the reaction is of first order. Temperature dependence of the rate was determined at constant initial concentration of the hydrodisulfide and summarized in Table IV.

TABLE IV
TEMPERATURE DEPENDENCE OF DECOMPOSITION RATES OF RSSH
(Concentration, 0.5 mole/l.)

Temp., °C.	100	110	120	130	140	150
k (sec.$^{-1}$ $\times$ 10^5)	0.18	0.47	0.78	1.54	2.29	4.41

Activation energy $E = 20.0$ kcal./mole and frequency factor $A = 1.01 \cdot 10^6$ were calculated from the values in Table IV. The same energy value was obtained from Fig. 2, where the decomposition was conducted in the absence of the solvent. The activation energy of the decomposition under irradiation of ultraviolet light was calculated from Fig. 3 in a temperature range from 60° to 120° to be 8.51 kcal./mole.
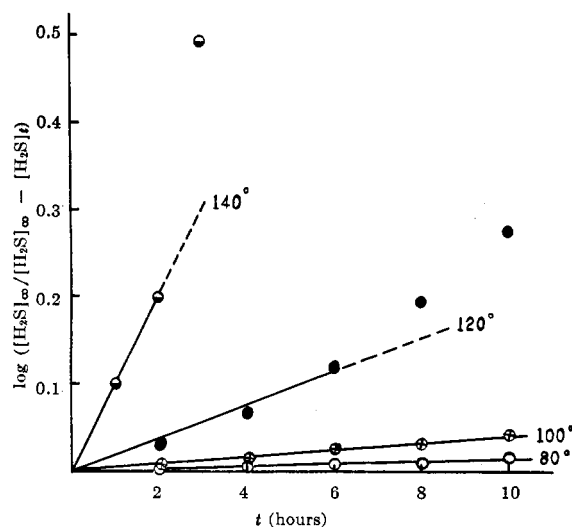

Fig. 2.—First-order plots for hydrogen sulfide formation in the dark.
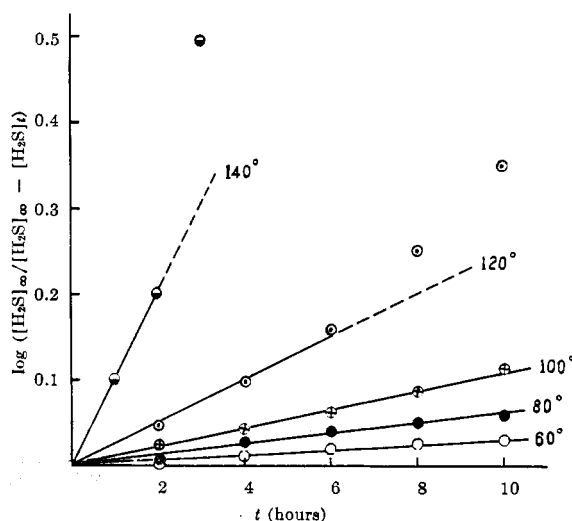No solvent was used

Fig. 3.—First-order plots for hydrogen sulfide formation under ultraviolet irradiation
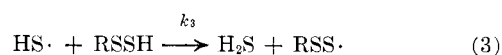No solvent was used.

Discussion

The effect of light on the decomposition suggests a free radical mechanism. A variety of investigators[3] is convinced that alkoxy radical is the immediate precursor for the further reaction steps in the reaction in which hydroperoxide participates. Analogies with decomposition of hydroperoxide[3] and of disulfide[6,7] also suggest a primary homolytic dissociation of the S—S bond into free radicals.

$$RSSH \xrightarrow{k_1} RS\cdot + \cdot SH \qquad (1)$$
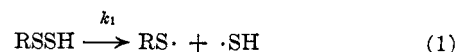
The previous paper[1] reported that even a stable free radical such as diphenylpicrylhydrazyl can easily abstract a hydrogen atom from the hydrodisulfide. Hydrogen abstraction reactions with liberation of free radicals (as above) must follow dissociation step 1.

(6) W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 42.

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, N. Y., 1957, p. 522.

$$\text{RS} \cdot + \text{RSSH} \xrightarrow{k_2} \text{RSH} + \text{RSS} \cdot \qquad (2)$$

$$\text{HS} \cdot + \text{RSSH} \xrightarrow{k_3} \text{H}_2\text{S} + \text{RSS} \cdot \qquad (3)$$

The previous paper[1] also reported that the dehydrogenated product from the aralkyl hydrodisulfide was diaralkyl tetrasulfide. The recombination of the same two free radicals as indicated in step 4 explains the formation of dibenzhydryl tetrasulfide.

$$2\text{RSS} \cdot \xrightarrow{k_4} \text{RSSSSR} \qquad (4)$$

The simplified steps 1 to 4 explain qualitatively the products obtained in the total decomposition cited in Table I. The much higher rate of step 2 or 3 than of step 1 was suggested in the previous paper[1] and indicates that step 1 must be rate-determining. Consideration of the rate-determining step leads to the conclusions that the rate of hydrogen sulfide evolution or rate of thiol formation is equal to k_1 and that the rate of hydrodisulfide decomposition is $3k_1$.

$$d[\text{H}_2\text{S}]/dt = d[\text{RSH}]/dt = k_1[\text{RSSH}]$$

$$-d[\text{RSSH}]/dt = 3k_1[\text{RSSH}]$$

The first-order rate constant k obtained above should represent $3k_1$. The over-all activation energy E and the frequency factor A calculated above should represent E_1 and A_1 respectively, where E_1 and A_1 signify activation energy and frequency factor of step 1. E_1 also represents the dissociation energy of the S—S bond in the hydrodisulfide. The literature reported the dissociation energy of the S—S bond in the dialkyl disulfide[7,8] to be in the range of 70–73 kcal./mole and that of 2,2'-dibenzothiazolyl disulfide[9,10] to be 29 and 32.7 kcal. The value obtained in the present study is considered reasonable.

Table II indicates that at an earlier stage of the reaction the amount of hydrogen sulfide approaches one third the amount of hydrodisulfide decomposed and that at a very early stage the amount of hydrogen sulfide is approximately equal to that of thiol. However, the amount of hydrogen sulfide surpasses that of the thiol as the reaction time increases. The result of total decomposition cited in Table I indicates a similar phenomenon. This may be interpreted by a subsidary step

$$\text{HS} \cdot + \text{RSH} \xrightarrow{k_5} \text{H}_2\text{S} + \text{RS} \cdot \qquad (5)$$
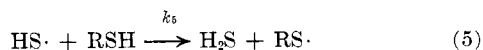
which occurs at the later stage, where the concentration of the thiol increases at the expense of the hydrodisulfide, although k_5 is far smaller than k_3 as suggested in the previous paper. Recombination of the radical RS· with another RS· or with RSS· may occur and give less polysulfide than tetrasulfide. However, the analytical methods are not so accurate to detect this. The deviation from linearity shown in Fig. 2 and Fig. 3 is considered due to the parallel occurrence of step 5 besides step 3.

It appears interesting to compare the decomposition of benzhydryl hydrodisulfide with that of dibenzhydryl

disulfide.[11] The latter compound decomposes at 180° to give thiobenzophenone, sym-tetraphenylethane, sulfur, and smaller amounts of hydrogen sulfide, dibenzhydryl mono- and polysulfides, diphenylmethane, and a trace of tetraphenylethylene. Diphenylmethanethiol was not found among the products. The mechanism of decomposition proposed is rather complex. Homolytic dissociations of the S—S bond and of the $(\text{C}_6\text{H}_5)_2$-CH—S bond are primary steps for further reaction. A hydrogen atom of the benzhydrylsulfenyl radical (C_6-$\text{H}_5)_2\text{CH—S}$· is abstracted with various free radicals present in the reaction system to yield thiobenzophenone. Dibenzhydryl tetrasulfide[12] was also reported to give similar products at 180°. In the present study the benzhydryl–sulfenyl radical is not dehydrogenated with the radical HS·, but dehydrogenates the hydrodisulfide yielding diphenylmethanethiol. However, a pale blue color was observed in the decomposition mixture of the hydrodisulfide at a higher temperature (150°) and at the later stage of the reaction. This indicates the formation of thiobenzophenone.

Comparison of the dissociation of the RS—SH bond with that of the RO—OH bond will be discussed below. Homolytic dissociation of the O—O bond of benzhydryl hydroperoxide was suggested to give benzophenone, benzhydrol and water in a paper[13] which reported the autoxidation of diphenylmethane. As compared with the decomposition of hydroperoxide in general, the following three factors cause the decomposition mechanism of the hydrodisulfide to be simple. (a) Owing to the hydrogen bond between the molecules,[14] the decomposition rate of the hydroperoxide was reported to depend on concentration. However, its absence between the hydrodisulfide molecules indicates the approximate constancy of a first-order rate over a certain range of initial concentration. (b) Very high rates of steps 2 and 3 protect the radical $(\text{C}_6\text{H}_5)_2\text{CHS}$· from being dehydrogenated to benzophenone. (c) The previous[1] and present papers indicate that the recombination step 4 is specific and present papers indicate that the recombination step 4 is specific for the radical RSS·, and generally speaking, specific for an organic polysulfenyl radical. As to the decomposition mechanism of hydroperoxide, t-butoxy radical librated from t-butyl hydroperoxide,[15] for example, dehydrogenates the hydroperoxide to give the t-butyl peroxy radical. The latter radicals recombine with each other, but result in yielding an oxygen molecule and t-butoxy radical, which in turn induce the decomposition. In contrast to the oxygen analog, the organic polysulfenyl radical is rather stable and recombines with each other without decomposition, because the recombined product, polysulfide, is also a stable compound.

(8) See ref. 6, p. 17.

(9) H. G. Cutforth and P. W. Selwood, J. Am. Chem. Soc., 70, 278 (1948).

(10) J. Tsurugi and H. Fukuda, Rubber Chem. Technol., 31, 788 (1958); H. Fukuda and J. Tsurugi, ibid., 34, 648 (1961).

(11)(a) J. Tsurugi and T. Nakabayashi, Nippon Kagaku Zasshi, 77, 578 (1956); Chem. Abstr., 52, 9047i (1958). (b) See also J. Tsurugi, Rubber Chem. Technol., 31, 762 (1958).

(12) J. Tsurugi and T. Nakabayashi, Nippon Kagaku Zasshi, 77, 583 (1956); Chem. Abstr., 52, 9048b (1958). See also 11b.

(13) F. Mashio and Y. Nakagawa, Kogyo Kagaku Zasshi, 55, 111 (1952); Chem. Abstr., 48, 6404i (1954).

(14) L. Bateman and H. Hughs, J. Chem. Soc., 4594 (1952). L. Bateman, H. Hughs, and A. L. Morris, Discussions Faraday Soc., 14, 190 (1953).

(15) E. R. Bell, J. H. Raley, F. F. Rust; F. H. Seubold, and W. E. Vaughan, Discussions Faraday Soc., 10, 246 (1951).