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The Reaction between Hydrocarbon and Hydrogen Sulfide in Silent Electrical Discharge. I. The Reaction of Ethylene or Propylene with Hydrogen Sulfide

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In order to examine the possibility of the direct introduction of the sulfhydryl radical into ethylene or propylene and that of the telomerization by means of a silent discharge, the mixture of ethylene or propylene and hydrogen sulfide was discharged in an ozonizer. (1) With ethylene and hydrogen sulfide, the main products were ethyl mercaptan, *n*-butyl mercaptan, and ethylene dithioglycol. Besides these compounds, the reaction products were confirmed to be diethyl sulfide, *s*-butyl, *n*-hexyl, *n*-propyl, and isopropyl mercaptans, and gaseous products. (2) With propylene and hydrogen sulfide, on the other hand, *n*-propyl mercaptan, di-*n*-propyl sulfide, isopropyl mercaptan, and 1,2-propylene dithioglycol were obtained as the main products. Besides these compounds, there were diisopropyl sulfide, ethyl and *n*-butyl mercaptans, 4-methyl-1-pentene, 2,3-dimethylbutane, 1,5-hexadiene, 2-methylpentane, 1-hexene, *n*-hexane, and gaseous products. The maximum yield of the liquid products was obtained when ethylene or propylene and hydrogen sulfide were mixed in approximately the ratio of 1:1. Judging from the relative concentration of each compound in the reaction products, it may be said that vinyl, ethyl, and sulfhydryl radicals in the reaction system of ethylene and hydrogen sulfide, and 2-methylvinyl, isopropenyl, propyl, allyl, isopropyl, and sulfhydryl radicals in the reaction system of propylene and hydrogen sulfide, are the main intermediates.

The oxidation of hydrocarbons by a silent electrical discharge has been studied by Sugino *et al.*[2] and by Tsutsumi *et al.*[3]

In previous papers,[4] the reaction between hydrocarbon (cyclohexane, ethylene, and propylene) and hydrogen cyanide in a silent discharge was studied. When a mixed gas of ethylene and hydrogen cyanide was discharged in an ozonizer under atmospheric pressure, acrylonitrile could be prepared in one step. Besides this compound, the formation of telomers, such as ethyl, *n*-butyl, and *n*-hexyl cyanides, was also observed. Moreover, the reactions of ethylene with 2-propanol and with carboxylic acid under a silent dis-

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1) Present address: Department of Chemistry, Faculty of Education, Kagawa University, Takamatsu.

2) K. Sugino and E. Inoue, This Bulletin, **24**, 93 (1951); K. Sugino and E. Inoue, *Nippon Kagaku Zasshi*, **75**, 10, 617 (1954); E. Inoue, *J. Electrochem. Soc. Jap.*, **22**, 668 (1954); E. Inoue, *ibid.*, **23**, 18, 76, 403, 452, 574, 648 (1955); E. Inoue and K. Sugino, *ibid.*, **24**, 33 (1956); K. Sugino, E. Inoue, K. Shirai, T. Koseki, and T. Gomi, *Nippon Kagaku Zasshi*, **86**, 114 (1965).

3) N. Sonoda, S. Yamamoto, K. Okumura, S. Noda, and S. Tsutsumi, "Oxidation of Organic Compounds," Vol. II, Advances in Chemistry Series 76, American Chemical Society, Washington (1968), pp. 352—362.

4) K. Kawamoto, N. Sonoda, and S. Tsutsumi, This Bulletin, **41**, 1376 (1968); K. Kawamoto, *ibid.*, **41**, 2161 (1968); K. Kawamoto and Y. Nishimura, *ibid.*, **42**, 1105 (1969).

charge have been reported by Hiraki.[5]

The direct synthesis of mercaptan and sulfide from olefin and hydrogen sulfide has been reported by many investigators. Vaughan and Rust[6] found that the photo-chemical addition of hydrogen sulfide to olefinic bonds took place very readily, giving mixtures of the corresponding mercaptans and sulfides. The radiation-induced addition of hydrogen sulfide to propylene to give *n*-propyl mercaptan and di-*n*-propyl sulfide has been investigated by Sugimoto *et al.*[7] The X-ray initiated free-radical addition of hydrogen sulfide to fluoroethylenes has been reported by Harris and Stacey.[8]

Losanitsch[9] reported that when a mixture of ethylene and hydrogen sulfide was subjected to a silent electrical discharge, ethyl mercaptan and the polymer of thioaldehyde ($(C_2H_4S)_6$) were obtained. However, no detailed study of the reaction of propylene with hydrogen sulfide under a silent discharge has yet been reported.

The present study was undertaken to find out whether the mercaptan and the sulfide are obtained by the reaction of ethylene or propylene with hydrogen sulfide under a silent discharge, to check whether or not a telomerization occurs under the present reaction conditions, and, at the same time to ascertain the mechanism of this reaction. In this research, the silent discharge was carried out in a Siemen ozonizer for 6 hr, using a voltage of 12 kilovolts. The direct introduction of a sulfhydryl radical into hydrocarbon was observed.

Experimental

Materials. The ethylene and propylene were purchased from the Nihon Sekiyu Kagaku Co., Ltd. (Kawasaki) and the Takachiho Chemicals Co. (Tokyo) respectively, and the hydrogen sulfide, from the Seitetsu Chemicals Co. (Osaka). These materials were used without further purification. No impurity was found in these reagents by gas-chromatographic analysis. (Columns of activated charcoal, acetonylacetone, dimethylsulfolane, and silica gel were used.)

Apparatus. The silent discharge reactor system used in this study is shown in Fig. 1. (1) Helium, hydrogen sulfide, and ethylene or propylene coming from the bomb were passed over calcium chloride (A). (2) The molar ratios of the ethylene or propylene and the hydrogen sulfide were roughly determined by means of a manometer (B), and the quantitative analysis of the mixed gas in this experiment was performed by gas chromatography. (A column of silica gel was used.) (3) The reservoirs (C) were filled with a mixture of ethylene or propylene and hydrogen sulfide. (4) The mixed gas was circulated by means of a pump (D) at the rate of 2 *l*/min. (5) The outside (a) of the discharge tube (E) was filled with water, and the inner tube (b), with a 3% $CuSO_4$ solution. (6) The discharge tube (E) used was a Pyrex tube 45 cm in effective length, 3.5 cm in outside diameter, and with a space gap of 0.25 cm. (7) The electrical energy was supplied by a 15-kV transformer (F).

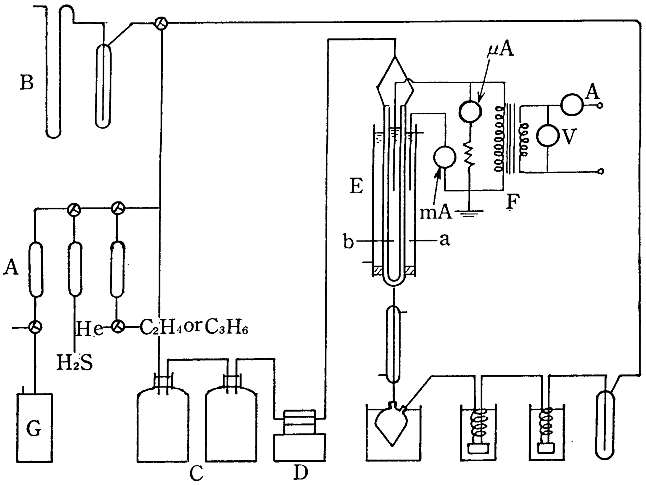

Fig. 1. Apparatus.

Procedure. In order to exclude the oxygen, the pressure in the system was reduced by means of a vacuum pump (G), and the oxygen was completely replaced by helium. In the presence of a small quantity of air, a great deal of a tarry yellow deposit was formed on the glass wall. A mixture of ethylene or propylene and hydrogen sulfide, at the molar ratio shown in Tables 1 and 3, was then put into the system. The volume of the system was 49.0 *l*. The mixed gas was made homogeneous by using a pump (D) for 30 min and was then passed through the discharge tube at a regular velocity of 2 *l*/min for the period of the reaction. A current of 60 cycles was passed through a voltage regulator; the voltage was stepped up by a transformer to give the required value. The products coming out of the discharge tube were condensed by passing them through a condenser; then they were collected by being passed through two traps cooled to −45°C by acetone-dry ice. The liquid products were analyzed by the method described below, while the non-condensable gases were analyzed by gas chromatography at intervals of 20 min. The pressure in the system during the period of the reaction was measured at intervals of 20 min.

Identification and Analysis of the Reaction Products. The liquid products obtained by the reaction between ethylene or propylene and hydrogen sulfide were identified by comparing their retention times on the gas chromatogram with those of authentic samples. (Columns of tricresyl phosphate, dinonyl phthalate, and Silicone DC-550 were used.) In addition, the reaction products were fractionally distilled, and the constituents of the fraction were identified by observing the formation of the derivatives.[10] Ethyl mercaptan was obtained in a fraction boiling at 33—36°C. From this fraction, 2,4-dinitrophenyl thioether, mp 114—115°C, and the 3,5-dinitrobenzoyl thioester, mp 61—62°C were obtained. The fraction boiling at 90—93°C was confirmed to consist mainly of diethyl sulfide by transforming it into the diethyl sulfone,[11] mp 73—74°C. Furthermore, the infrared spectrum of this fraction agreed with that of the authentic diethyl sulfide. *n*-Butyl mercaptan, obtained as a fraction boiling at 96—100°C, was converted into its 2,4-dinitrophenyl thioether and the 3,5-dinitrobenzoyl thioester, the melting points of the derivatives being 65—66°C and 48—49°C respectively. The ethylene dithioglycol was obtained in a fraction boiling at 144—146°C. Upon gas-chromatographic analysis, this frac-

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[5] T. Hiraki, *ibid.*, **42**, 1981, 2993, 3216 (1969).

[6] W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**, 472 (1942).

[7] K. Sugimoto, W. Ando, and S. Oae, This Bulletin, **37**, 365 (1964).

[8] J. F. Harris, Jr., and F. W. Stacey, *J. Amer. Chem. Soc.*, **85**, 749 (1963).

[9] S. M. Losanitsch, *Ber.*, **40**, 4656 (1907).

[10] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Amer. Chem. Soc.*, **54**, 1985 (1932); E. Wertheim, *ibid.*, **51**, 3662 (1929).

[11] E. O. Beckmann, *J. Prakt. Chem.*, (2), **17**, 439 (1878).

tion showed the same retention time as that of authentic ethylene dithioglycol. The infrared spectrum of this fraction agreed with that of the authentic specimen.

The liquid products obtained by the reaction between propylene and hydrogen sulfide were identified by the following method. The fraction boiling at 56—60°C consisted of isopropyl mercaptan, which was identified by transforming it into the 2,4-dinitrophenyl thioether, mp 94—94.5°C, and the 3,5-dinitrobenzoyl thioester, mp 83—84°C. *n*-Propyl mercaptan was present in a fraction boiling at 65—68°C. From this fraction, the 2,4-dinitrophenyl thioether, mp 80—81°C, and the 3,5-dinitrobenzoyl thioester, mp 51—52°C were obtained. Di-*n*-propyl sulfide, obtained as a fraction boiling at 140—143°C, and 1,2-propylene dithioglycol (bp 148—154°C) showed the same retention times on the gas chromatogram as those of the authentic reagents, furthermore, the infrared spectra of these fractions agreed with those of the authentic specimens. The liquid hydrocarbon products listed in Table 4 were identified by the use of squalane, β,β'-oxydipropionitrile, tricresyl phosphate, and dimethylsulfolane columns.

These derivatives showed no depression of their melting points when mixed with authentic specimens. The gaseous products, obtained by the reaction between ethylene or propylene and hydrogen sulfide, were also analyzed by gas chromatography. (Columns of activated charcoal, tricresyl phosphate, a mixture of molecular sieve 13 X and hexamethylphosphoramide, acetonylacetone, and dimethylsulfolane were used.) The gaseous products could not be determined quantitatively. The quantitative analysis of the liquid products in this experiment was performed by gas chromatography.

Results and Discussion

The results obtained by running ethylene with hydrogen sulfide in an ozonizer under the conditions described in Table 1 are summarized in Table 2. Further, by running propylene with hydrogen sulfide under the conditions listed in Table 3, a large number of compounds were obtained. The compositions of those compounds which have been identified are summarized in Table 4. The percentage of the compounds shown in these tables does not necessarily represent the maximum yield, but is an average of three experiments under constant operating conditions. However, the fluctuation in the yields of the compounds obtained in repeated experiments was less than 1 per cent. A small amount of air was found to reduce the liquid products.

Table 1. The reaction between ethylene and hydrogen sulfide in silent electrical discharge
(Experimental conditions)

Experiment No.	1	2	3	4	5
Second. voltage (kV)	12	12	12	12	12
Second. current (mA)	1.9	2.0	2.1	2.1	2.2
Temp. of discharge tube (°C)					
Inside	17—39	20—49	20—52	19—49	16—47
Outside	17—32	20—42	20—45	19—41	16—40
Discharge time (hr)	6	6	6	6	6
Materials used (*l*)					
Ethylene	40.8	35.0	27.2	19.6	14.0
Hydrogen sulfide	8.2	14.0	21.8	29.4	35.0
Molar ratio (C_2H_4/H_2S)	4.9	2.5	1.3	0.7	0.4

Table 2. The reaction between ethylene and hydrogen sulfide in silent electrical discharge
(Experimental results)

Experiment No.	1	2	3	4	5
Liquid product collected (g)	1.43	4.92	8.54	7.00	4.74
Conversion efficiency[a] (%)	2.3	7.6	12.7	10.1	6.7
Composition of liquid reaction products[b] (%)					
Ethyl mercaptan	62.1	62.6	62.7	61.6	60.8
n-Butyl mercaptan	18.3	13.0	7.5	3.5	3.2
s-Butyl mercaptan	0.4	0.3	0.2	0.1	0.1
Ethylene dithioglycol	3.1	9.2	15.6	24.2	25.2
Diethyl sulfide	3.1	2.8	2.4	1.7	1.2
n-Propyl mercaptan	4.5	4.3	4.1	3.9	3.9
Isopropyl mercaptan	0.9	0.6	0.5	0.5	0.4
n-Hexyl mercaptan	T	T	T	T	T
Unidentified product	7.6	7.2	7.0	4.5	5.2

T: Trace

a) The conversion efficiency was given by (grams of reaction product/grams of materials (ethylene+hydrogen sulfide) used) × 100.

b) The yields of each compound produced were given by (grams of each compound/grams of total reaction product) × 100.

Table 3. The reaction between propylene and hydrogen sulfide in silent electrical discharge
(Experimental conditions)

Experiment No.	6	7	8	9
Second. voltage (kV)	12	12	12	12
Second. current (mA)	1.9	1.9	1.9	2.0
Temp. of discharge tube (°C)				
Inside	19—44	14—45	15—46	18—46
Outside	19—39	14—40	15—40	18—41
Discharge time (hr)	6	6	6	6
Materials used (*l*)				
Propylene	37.7	28.0	21.3	16.3
Hydrogen sulfide	11.3	21.0	27.7	32.7
Molar ratio (C_3H_6/H_2S)	3.3	1.3	0.8	0.5

Table 4. The reaction between propylene and hydrogen sulfide in silent electrical discharge
(Experimental results)

Experiment No.	6	7	8	9
Liquid product collected (g)	4.18	6.20	6.93	6.08
Conversion efficiency (%)	4.8	7.3	8.4	7.6
Composition of liquid reaction products (%)				
n-Propyl mercaptan	49.4	57.5	56.5	48.3
Isopropyl mercaptan	10.2	12.2	11.3	10.4
Di-*n*-propyl sulfide	14.8	5.7	3.9	2.8
Diisopropyl sulfide	4.2	1.8	1.2	0.8
1,2-propylene dithioglycol	3.6	5.8	10.9	20.4
Ethyl mercaptan	3.0	2.0	1.2	0.7
n-Butyl mercaptan	0.6	0.7	0.3	0.2
4-Methyl-1-pentene	0.3	0.2	0.1	0.1
2,3-Dimethylbutane	0.2	0.1	0.1	T
1,5-Hexadiene	0.1	0.1	T	T
2-Methylpentane	0.1	T	T	T
1-Hexene	T	T	T	T
n-Hexane	T	T	T	T
Unidentified product	13.5	13.9	14.5	16.3

Air apparently acts as a free radical scavenger to retard this chain reaction. The gaseous products given by the reaction of ethylene and hydrogen sulfide consisted of hydrogen, methane, ethane, acetylene, propane, propylene, *n*-butane, 1-butene, and 1,3-butadiene. In the cases of propylene and hydrogen sulfide, the gaseous products were found to be hydrogen, methane, ethane, ethylene, acetylene, propane, methylacetylene, and allene.

Influence of the Molar Ratio of Ethylene to Hydrogen Sulfide on the Yield. In order to check the molar-ratio effects on the discharge reaction of ethylene and hydrogen sulfide, the reaction was carried out with various ratios of the ethylene to the hydrogen sulfide, as is shown in Table 1. As may be seen from Table 2, the yield of the reaction product depends upon the molar ratio of the ethylene and the hydrogen sulfide; the maximum yield of liquid products was obtained when they were mixed in the ratio of approximately 1: 1. However, the distribution of the products depends on the molar ratio of the reactants as follows: (1) The yield of ethylene dithioglycol increased at high ratios of hydrogen sulfide to ethylene. (2) On the other hand, the *n*-butyl mercaptan and diethyl sulfide decreased with an increase in the ratio of hydrogen sulfide to ethylene. (3) The yield of ethyl mercaptan, though the molar ratio of ethylene and hydrogen sulfide changed, was approximately constant. Ethyl, *n*-butyl, and *n*-hexyl mercaptans seem to be formed by the telomerization between ethylene and hydrogen sulfide. However, the formation of *n*-octyl mercaptan (1: 4 telomer) and one-to-five or more products could not be observed by gas-chromatographic analysis. The total pressure in the reaction system was measured at intervals of 20 min; the results are shown in Fig. 2.

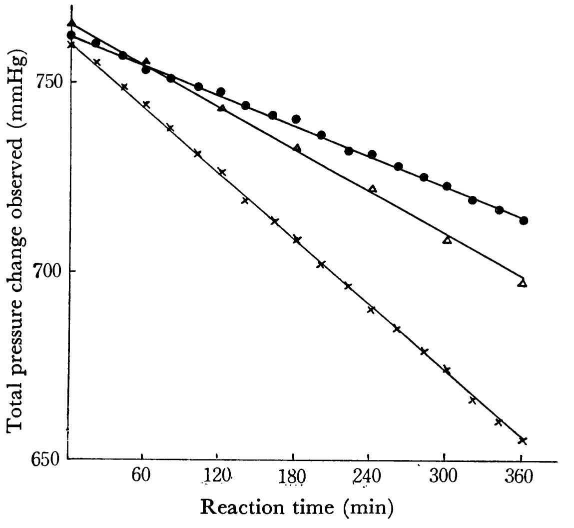


Fig. 2. Relation between total pressure in reaction system and time of reaction. (Reactants: C_2H_4 and H_2S)

As may be seen from this graph, the total pressure decreased linearly with the progress of the reaction time, in spite of the molar ratios of ethylene and hydrogen sulfide. A proportional relation was found between the velocity of the reduced pressure in the reaction system and the yield of the reaction product; that is, it has been found that increasing the velocity of the reduced pressure increases the amount of the reaction product. In addition, the ratio of the consumption of ethylene to hydrogen sulfide was found, from gas analysis, to be kept constant during the period of the reaction.

The Reaction between Propylene and Hydrogen Sulfide. When a mixture of propylene and hydrogen sulfide was allowed to react in a silent discharge, a large number of products (summarized in Table 4) were obtained. As is shown in Table 4, the conversion efficiency (grams of reaction product per grams of propylene and hydrogen sulfide used ×100) depends upon the ratio of propylene to hydrogen sulfide; it has been found that the maximum yield of the liquid product was obtained when the mixed components of the reactant were approximately in the ratio of 1: 1, that, in the 1: 1 ratio, the addition products, such as *n*-propyl mercaptan and isopropyl mercaptan, were obtained in high yileds, while such sulfides as di-*n*-propyl sulfide and diisopropyl sulfide decreased with an increase in the ratio of hydrogen sulfide to propylene, and that, on the other hand, the yield of 1,2-propylene dithioglycol increased at high ratios of hydrogen sulfide to propylene. The formation of allyl mercaptan could not be observed by gas-chromatographic analysis. The yield of *n*-propyl mercaptan was higher than that of isopropyl mercaptan. Therefore, the addition followed an anti-Markownikoff rule. This rule was observed in both the photo-chemical addition$^{6)}$ and the radiation-induced addition$^{7)}$ of hydrogen sulfide to propylene. The nature of the discharge-induced addition appears to be similar to that of these additions. Figure 3 shows how the total pressure in the reaction system changes during the period of the silent discharge. In the cases of propylene and hydrogen sulfide, the same results as in the case of ethylene were obtained.

The Mechanism of the Formation of the Main Products Obtained by the Reaction of Ethylene and Hydrogen Sulfide.

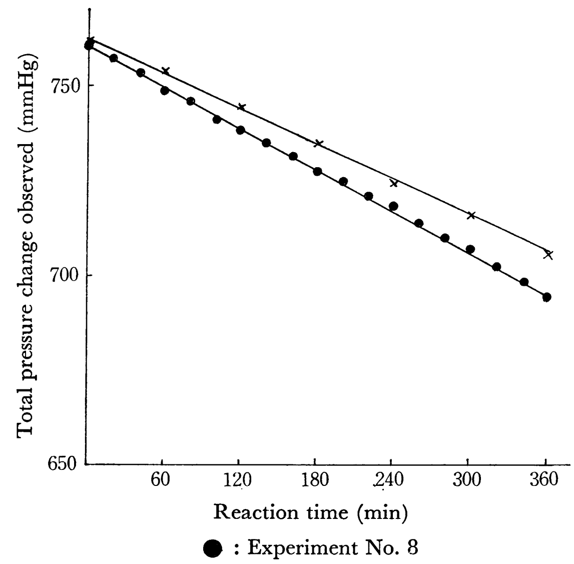
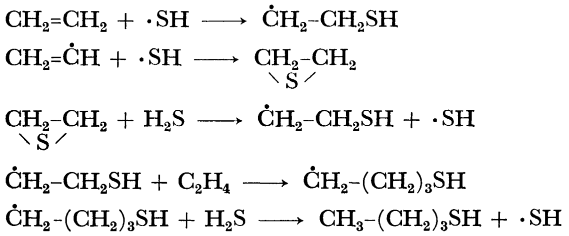


Fig. 3. Relation between total pressure in reaction system and time of reaction. (Reactants: C_3H_6 and H_2S)

It was reported by Egloff *et al.*[12] that the radical from ethylene in the electrical discharge was a vinyl radical, and that it was produced by breaking a carbon-hydrogen bond. Tsutsumi[13] reported that the vinyl radical was obtained by two molecular processes,[14] as is shown below. One of the present authors reported that the formation of acrylonitrile by the reaction of ethylene with hydrogen cyanide in the silent discharge may be observed by a combination of the vinyl radical and the cyano radical.[4] It has been reported by Hiraki[5] that the formation of the methyl vinyl ketone by a reaction between ethylene and methyl acetate in a silent discharge may be due to the combination of the vinyl radical and acetyl radical. Gorden and Ausloos[15] reported that the vacuum-ultraviolet photolysis of ethylene led essentially to three types of processes, as is indicated below.[16]

The mechanism of the formation of ethyl mercaptan, *n*-butyl mercaptan, ethyl dithioglycol, and diethyl sulfide by the reaction of ethylene with hydrogen sulfide may be represented as follows: The first step is the vibrational excitation of the ethylene molecule and the hydrogen sulfide molecule by electron impact,[17] while the second step consists of both (1) the reaction of the excited ethylene molecule with a normal ethylene molecule to give the vinyl radical and the ethyl radical,[14] and(2) the decomposition of the excited molecules to give the vinyl radical, the sulfhydryl radical, and the hydrogen atom. Ethyl mercaptan may be formed by three paths: (1) the combination of the ethyl radical (obtained by two molecular processes) and the sulfhydryl radical, (2) the reaction of the sulfhydryl radical with ethylene, and then the addition of a hydrogen atom to the $\dot{C}H_2$-CH_2SH radical so formed, and (3) the formation of vinylthiol[18] or ethylene sulfide[19] by the combination of the vinyl radical and the sulfhydryl radical, and then the addition of hydrogen atoms to the compounds thus obtained. The formation of acetylene, 1,3-butadiene, and 1-butene may show the existence of the vinyl radical. Further, it seems that ethane, *n*-butane, and 1-butene are obtained by the use of the ethyl radical. The formation of *n*-butyl mercaptan may be presented as follows:



$$CH_2{=}CH_2 + \cdot SH \longrightarrow \dot{C}H_2\text{-}CH_2SH$$
$$CH_2{=}\dot{C}H + \cdot SH \longrightarrow \underset{\diagdown S \diagup}{CH_2\text{-}CH_2}$$
$$\underset{\diagdown S \diagup}{CH_2\text{-}CH_2} + H_2S \longrightarrow \dot{C}H_2\text{-}CH_2SH + \cdot SH$$
$$\dot{C}H_2\text{-}CH_2SH + C_2H_4 \longrightarrow \dot{C}H_2\text{-}(CH_2)_3SH$$
$$\dot{C}H_2\text{-}(CH_2)_3SH + H_2S \longrightarrow CH_3\text{-}(CH_2)_3SH + \cdot SH$$

Ethyl dithioglycol may be formed by the addition of the sulfhydryl radical to the $\dot{C}H_2$–CH_2SH radical. The formation of diethyl sulfide may proceed by two paths: (1) the reaction between vinylthiol or ethylene sulfide and the hydrogen atom, the addition of the $CH_3CH_2S\cdot$ radical thus obtained to ethylene and then the reaction of the $CH_3CH_2SCH_2\dot{C}H_2$ radical and the hydrogen atom, and (2) the reaction of the ethyl mercaptan, once formed, with ethylene to give the diethyl sulfide.[20]

The Mechanism of the Formation of the Main Products Obtained by the Reaction of Propylene and Hydrogen Sulfide. The formation of the main products obtained by the reaction of propylene and hydrogen sulfide in a silent discharge is thought to proceed by a mechanism similar to that proposed for the reaction between ethylene and hydrogen sulfide. The process consists of both (1) the reaction of the excited propylene molecule with a normal propylene molecule to give 2-methylvinyl, isopropenyl, allyl, propyl, and isopropyl radicals,[21] and (2) the decomposition of the excited propylene or hydrogen sulfide to give 2-methylvinyl, isopropenyl, allyl,

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[12] C. L. Thomas, C. Egloff, and J. C. Morell, *Chem. Rev.*, **28**, 1 (1941).

[13] S. Tsutsumi, *Kagaku Kogyo*, **16**, 623 (1965).

[14] $CH_2{=}CH_2 + e^* \longrightarrow CH_2{=}CH_2{}^* + e$
$CH_2{=}CH_2{}^* + CH_2{=}CH_2 \longrightarrow CH_2{=}\dot{C}H + CH_3\dot{C}H_2$

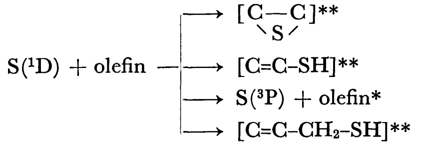
[15] R. Gorden, Jr., and P. Ausloos, *J. Chem. Phys.*, **47**, 1799 (1967).

[16] $C_2H_4{}^* \longrightarrow C_2H_2 + H_2$
$C_2H_4{}^* \longrightarrow C_2H_3 + H$
$C_2H_4{}^* \longrightarrow C_2H_2 + 2H$

[17] Although ion-molecular process are possible in some electron-impact reactions, in the present case this process does not seem to be the main path, judging from the results presented by Devins *et al.*, Inoue,[2] and Egloff *et al.*[12] The present reaction is presumed to be mostly a radical reaction. (J.C. Devins and M. Burton, *J. Amer. Chem. Soc.*, **76**, 2618 (1954).)

[18] Stacey *et al.* reported the preparation of vinylthiols by the X-ray-initiated addition of hydrogen sulfide to mono- and disubstituted acetylenes at room temperature, and it has been reported by Oae that vinylthiol is more stable than thioaldehyde. (F. W. Stacey and J. F. Harris, Jr., *J. Amer. Chem. Soc.*, **85**, 963 (1963); S. Oae, "Chemistry of Organic Sulfur Compounds," Kagakudojin, Kyoto (1968), p. 103.)Strausz *et al.* found that irradiation by a medium-pressure mercury arc lamp of mixtures of hydrogen sulfide and acetylene or methylacetylene in quartz reaction cells at −78° C gave good yields of vinyl mercaptan and 2-methylvinyl mercaptan respectively. (O. P. Strausz, T. Hikida, and H. E. Gunning, *Can. J. Chem.*, **43** (3), 717 (1965).)

[19] It was reported by Strausz *et al.* that, when a photo-chemical reaction between ethylene or propylene and carbonyl sulfide was carried out, the corresponding vinylthiols, such as vinyl mercaptan, methylvinyl mercaptan, and propenethiol, and the corresponding cyclic compounds, such as ethylene sulfide, and propylene sulfide, were formed. Furthermore, they reported that the following steps must be considered for the primary reaction:



$$S(^1D) + \text{olefin} \longrightarrow \begin{cases} [\underset{\diagdown S \diagup}{C\text{—}C}]^{**} \\ [C{=}C\text{-}SH]^{**} \\ S(^3P) + \text{olefin}^* \\ [C{=}C\text{-}CH_2\text{-}SH]^{**} \end{cases}$$

(O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.*, **84**, 4080 (1962); H. A. Wiebe, A. R. Knight, O. P. Strausz, and H. E. Gunning, *ibid.*, **87**, 1443 (1965).)

[20] The free radical addition of thiols to olefin under irradiation with gamma rays has been investigated by Fontijn and Spinks, and by Araki. They found that the corresponding sulfides were formed as the main products. (A. Fontijn and J. W. J. Spinks, *Can. J. Chem.*, **35**, 1384, 1397, 1410 (1957); K. Araki, *Nippon Kagaku Zasshi*, **81**, 807 (1960).) It has been reported by Bach that the processes induced by the discharge reaction are similar to those induced by radiolysis. (N. Bach, *Chem. Eng. Progr.*, **51**, 478 (1955).)

[21] $CH_2{=}CH\text{-}CH_3 + e^* \longrightarrow C_3H_6{}^* + e$

$$C_3H_6{}^* + CH_2{=}CH\text{-}CH_3 \longrightarrow \begin{cases} \dot{C}H{=}CH\text{-}CH_3 \\ CH_2{=}\dot{C}\text{-}CH_3 \\ CH_2{=}CH\text{-}CH_2\cdot \end{cases} + \begin{cases} CH_3\text{-}CH_2\text{-}CH_2\cdot \\ CH_3\text{-}\dot{C}H\text{-}CH_3 \end{cases}$$

and sulfhydryl radicals, and a hydrogen atom.[22] The formation of *n*-propyl mercaptan may be represented by the same mechanism as the formation of ethyl mercaptan in the case of ethylene. In the case of the reaction between propylene and hydrogen sulfide, vinylthiols ($CH_3CH{=}CHSH$ and $CH_3C(SH){=}CH_2$) or propylene sulfide ($\mathrm{CH_3{-}\underbrace{CH{-\!-}CH_2}_{S}}$) may be formed by the combination of the 2-methylvinyl radical or the isopropenyl radical and the sulfhydryl radical.

Isopropyl mercaptan may be formed by two paths: (1) A hydrogen atom adds preferentially to the terminal carbon atom of propylene to form the isopropyl radical,[23] and the radical thus produced yields isopropyl mercaptan. (2) This compound is obtained by the addition of hydrogen atoms to vinylthiols or propylene sulfide.

The dimeric products, such as 4-methyl-1-pentene, 2,3-dimethylbutane, 2-methylpentane, 1,5-hexadiene, 1-hexene, and *n*-hexane, may be formed by a recombination reactions between propyl, isopropyl, and allyl radicals.

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[22] $$C_3H_6^* \longrightarrow \left\{\begin{array}{l} \dot{C}H{=}CH{-}CH_3 \\ CH_2{=}\dot{C}{-}CH_3 \\ CH_2{=}CH{-}CH_2\bullet \end{array}\right. + \bullet H$$

$$H_2S^* \longrightarrow \bullet SH + \bullet H$$

[23] Moore reported that, when the mercury-photosensitized hydrogenation of propylene was carried out over a range of temperatures from 30 to 200°C, a hydrogen atom was added to the terminal carbon atom of propylene to form the isopropyl radical. (W. J. Moore, *J. Chem. Phys.*, **16**, 916 (1948).)