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The Reaction between Hydrocarbon and Hydrogen Chloride in Silent Electrical Discharge. I. The Reaction of Ethylene with Hydrogen Chloride

Kazuaki Kawamoto, Keiko Tamura, and Setsuko Hikasa
Institute of Commodities, Faculty of Economics, Kagawa University, Takamatsu, Kagawa 760
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Silent discharge was found to induce the reaction of ethylene and hydrogen chloride and to give mainly addition and telomerization products. Discharge on a mixture of ethylene and hydrogen chloride in an ozonizer under atmospheric pressure gave chloroethane, 1-chlorobutane, and 1,4-dichlorobutane as the main products. Besides these compounds, chloroethylene, 2-chlorobutane, 1,3-dichlorobutane, 2,3-dichlorobutane, 1,2-dichlorobutane, 1-chlorohexane, 1,2-dichloroethane, and gaseous products were also formed. The maximum yield of the liquid products was obtained when ethylene and hydrogen chloride were mixed in the ratio of approximately 1: 1. The formation of telomers was favored by a low ratio of the hydrogen chloride to the ethylene concentration, and by a low temperature in the discharge reaction. On the other hand, gaseous products increased with the rise in the discharge temperature and with an increase in the ratio of ethylene to hydrogen chloride. Judging from the product distribution, the reaction may be explained in terms of radical reactions involving vinyl, ethyl, and chlorine radicals. Among the reactions between ethylene and HX, such as hydrogen cyanide, hydrogen sulfide, and hydrogen chloride, the highest conversion was obtained by using the hydrogen chloride as the reactant.

In recent years, the oxidation of hydrocarbons in silent electrical discharge has been studied by Sugino *et al.*[1]

In particular, the reactions of ethylene with ammonia or oxygen in silent electrical discharge have been reported by them and by Tsutsumi *et al.*[2]

In previous papers,[3] the reactions of a hydrocarbon (ethylene, propylene, and cyclohexane) with hydrogen cyanide, and of a hydrocarbon (ethylene and propylene) with hydrogen sulfide in a silent discharge were reported. When a mixture of ethylene and hydrogen cyanide was discharged in an ozonizer, acrylonitrile could be prepared in one step. Besides this compound, the formation of telomers was observed. Moreover, when a mixture of ethylene and hydrogen sulfide was discharged in an ozonizer, the formation of such telomers as ethanethiol and 1-butanethiol was also observed.

The reaction of ethylene with hydrogen halide has been reported by many investigators. The photochemical addition of hydrogen bromide to olefins has been investigated by Vaughan *et al.*[4] Hanford *et al.*[5] reported the formation of mixtures of straight chain primary alkyl chlorides, ranging from chloroethane to greases and waxes, by the reaction between ethylene and hydrogen chloride in the presence of catalysts and water at a high temperature under a high pressure. It was recognized by Raley *et al.*[6] that the vapor-phase addition of hydrogen chloride to ethylene, as initiated by ultraviolet light or peroxide, yielded chloroethane and small amounts of hydrogen and ethane.

Moreover, it was found by Ford *et al.*[7] that when the reaction of ethylene with hydrogen chloride was carried out in the presence of free-radical initiators and water under ethylene pressures of 100—1000 atm, telomerization took place. The radiation-induced addition of hydrogen chloride to ethylene produced 1-chlorobutane and chloroethane, and this reaction was supposed to be a vapor-phase radical chain reaction.[8] No detailed study of the interaction of ethylene and hydrogen chloride in the silent discharge has yet been reported.

The present study was undertaken to find out whether or not the direct formation of such chloro compounds as chloroethylene, chloroethane, and 1-chlorobutane results from the reaction of ethylene with hydrogen chloride in a silent electrical discharge. Moreover, the differences among the reactions of ethylene with hydrogen cyanide, with hydrogen sulfide, and with hydrogen chloride were discussed. In this research, the silent discharge was carried out in a Siemens ozonizer for 8 h, using a voltage of 15 kV.

Experimental

Materials. The ethylene was purchased from the Nihon Sekiyu Co., Ltd. (Kawasaki), the hydrogen chloride, chloroethylene, and chlorine from the Seitetsu Chemicals Co. (Osaka), and chloroethane from the Tokyo Kasei Co. (Tokyo). These materials were used without further purification. No impurity was found in these reagents by gas chromatographic analysis. (Columns of activated charcoal, Silica gel, and Silicone GE SF-96 were used.)

Apparatus. In this experiment, the apparatus illustrated in Fig. 1 was used. (1) Helium, hydrogen chloride, and ethylene coming from each bomb were passed over calcium chloride (A). (2) The molar ratios of ethylene, hydrogen chloride, chloroethane, chloroethylene, and chlorine were

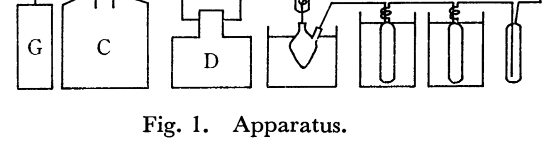

Fig. 1. Apparatus.

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 Silicone GE SF-96 was used.) (3) The reservoir (C) was filled with a mixture of ethylene, hydrogen chloride, and helium. (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% copper sulfate solution. (6) The discharge tube (E) used was a Pyrex tube 25 cm in effective length, 3 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).

Procedure. Air in the system was completely replaced by helium, by repeated evacuation and introduction of helium. The volume of the reaction system was 20.7 l. As a diluent, one-third volume (about 6.9 l) of helium was put into the reaction system, then a mixture of ethylene and hydrogen chloride (chloroethane, chloroethylene, and chlorine) at the molar ratios shown in Tables 1, 3, and 5 was put into it. 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 and 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 at −50 °C or −70 °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 30 min. The pressure in the system during the period of the reaction was measured at intervals of 30 min.

Identification and Analysis of the Reaction Products. The liquid products obtained by these reactions were identified by comparing their retention times on the gas chromatogram with those of authentic samples. (Columns of tricresyl phosphate, Silicone GE SF-96, Silicone DC 550). In addition, the reaction products were fractionally distilled, and the constituents of the fraction were identified by examining the infrared spectrum. The gaseous products obtained by these reactions were also analyzed by gas chromatography. (Columns of activated charcoal, tricresyl phosphate, silica gel, and Silicone GE SF-96). 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 chloride in an ozonizer under the conditions described in Tables 1 and 3 are summarized in Tables 2 and 4, respectively. Further, the results obtained by the reactions of chloro compounds with and without ethylene under the conditions listed in Table 5 are summarized in Table 6. The yields of each compound shown in these tables are an average of three experiments under constant operating conditions. The fluctuation in the yields of the compounds obtained in repeated experiments was less than 1 per cent. The gaseous products given by the reaction of ethylene and hydrogen chloride consisted of hydrogen, chlorine, methane, ethane, acetylene, propane, propylene, butane, 1-butene, and 1,3-butadiene.

Influence of the Molar Ratio of Ethylene to Hydrogen Chloride. As can be seen in Table 2, the yield of the reaction products depends upon the molar ratio of ethylene to hydrogen chloride; when the mixed components of the reactant were approximately in the ratio of 1: 1, the maximum yield of the liquid reaction products was obtained. However, the product distribution depended upon the molar ratio of the reactants as follows: (1) In the case of the range of discharge temperatures from 5 to 50 °C, when ethylene and hydrogen chloride were mixed in the ratio of approximately 1: 1, the proportion of chloroethane in the liquid products was at its maximum. (2) On the other hand, 1-chlorobutane decreased with the increase in the ratio of hydrogen chloride to ethylene. Thus, it may be said that the yield of telomer with $n=2$ is favored by a low ratio of the hydrogen chloride to the ethylene concentration. (3) The yields of dichloro and trichloro compounds of butane increased with the increase in the ratio of the hydrogen chloride to the ethylene. (4) A small amount of dichloro compounds of ethane were obtained, and their yields increased slightly with an increase in the ratio of the hydrogen chloride to the ethylene. (5) When the discharge reaction was performed at a higher ratio of the hydrogen chloride to the ethylene, a solid black deposit was formed on the wall of discharge tube, and the yield of the solid product thus obtained increased with a rise in the discharge temperature. Chloroethane, 1-chlorobutane, and 1-

Table 1. Influences of the molar ratio of ethylene to hydrogen chloride and of the discharge temperature on the yield of reaction products (Experimental conditions)

Experiment No.	1	2	3	4	5	6	7	8	9	10	11	12
Materials used (l)												
Ethylene	5.45	7.66	9.67	5.11	7.56	9.81	4.70	7.39	9.70	3.95	7.67	10.01
Hydrogen chloride	8.26	6.08	4.17	8.64	6.05	3.93	8.93	6.49	4.06	9.72	6.00	3.81
Molar ratio (C_2H_4/HCl)	0.65	1.26	2.26	0.59	1.26	2.44	0.53	1.14	2.39	0.42	1.26	2.65
Temp. of discharge tube (°C)												
Inside	5—27	5—26	5—25	25—45	25—45	25—46	50—76	50—76	50—76	75—94	75—95	75—98
Outside	5	5	5	25	25	25	50	50	50	75	75	75
Discharge time (h)	8	8	8	8	8	8	8	8	8	8	8	8
Second voltage (kV)	15	15	15	15	15	15	15	15	15	15	15	15
Second current (mA)	2.5	2.5	2.4	2.7	2.7	2.6	2.9	3.0	3.1	3.1	3.2	3.1

Table 2. Influences of the molar ratio of ethylene to hydrogen chloride and of the discharge temperature on the yield of reaction products (Experimental results)

Experiment No.	1	2	3	4	5	6	7	8	9	10	11	12
Liquid product collected (g)	10.27	12.09	9.59	10.39	13.52	11.76	9.86	12.53	11.82	9.71	11.04	11.55
Conversion efficiency[a] (%)	50.7	62.0	50.8	50.8	70.0	64.0	48.3	63.3	63.0	46.7	57.0	61.7
Composition of liquid reaction products[b] (%)												
Chloroethylene	T	1.0	1.4	T	1.3	2.0	T	0.9	1.5	T	0.7	1.4
Chloroethane	28.7	50.6	46.2	29.0	58.2	53.5	28.6	61.1	54.7	30.5	55.5	57.6
1-Chlorobutane	8.6	16.6	23.2	8.3	12.9	17.5	8.0	11.8	16.7	7.5	11.7	15.4
2-Chlorobutane	4.6	2.9	2.1	5.2	2.9	2.0	4.8	3.2	2.0	4.8	3.5	1.7
1,4-Dichlorobutane	22.1	16.3	15.2	18.0	13.0	11.2	14.5	11.2	9.7	12.2	10.7	8.2
1,3-Dichlorobutane	7.6	3.4	1.4	8.2	3.4	1.4	8.5	3.5	1.5	8.7	5.1	1.6
2,3-Dichlorobutane	6.1	1.4	0.2	6.9	1.5	0.8	8.7	1.6	1.0	9.2	1.9	1.2
1,2-Dichlorobutane	5.5	0.2	T	6.2	0.2	T	8.6	0.4	T	9.1	0.9	T
1-Chlorohexane	2.4	0.4	T	2.0	0.4	T	1.9	0.4	T	1.7	0.4	T
1,1-Dichloroethane	2.4	0.5	0.4	2.0	0.4	0.3	2.3	0.4	0.4	1.9	0.4	0.3
1,2-Dichloroethane	4.8	1.9	1.3	4.0	1.3	1.1	4.0	1.2	0.8	3.7	1.2	0.6
1,2,4-Trichlorobutane	3.5	0.2	0	5.1	0.4	0	6.7	0.5	0	6.9	0.8	0
1-Chloropropane	0.6	1.2	2.1	0.7	1.1	2.2	0.6	1.0	2.3	0.6	1.2	2.0
2-Chloropropane	0.5	0.6	0.9	0.6	0.8	1.0	0.5	0.8	1.0	0.5	1.0	1.0
1,2-Dichloropropane	0.9	0.2	T	0.9	0.2	T	1.0	0.2	T	1.0	0.3	T
1,3-Dichloropropane	1.7	0.2	T	1.4	0.2	T	1.3	0.2	T	1.3	0.2	T
1-Butene	T	0.4	2.0	T	0.4	2.4	T	0.5	2.8	T	0.9	3.0
Butane	T	0.5	2.1	T	0.5	2.5	T	0.7	2.9	T	1.0	3.1
1,3-Butadiene	T	0.3	1.5	T	0.3	2.1	T	0.4	2.7	T	0.7	2.9
Unidentified products	T	1.2	T	1.5	0.6	T	T	T	T	0.4	1.9	T

T: Trace. a) The conversion efficiency was given by (grams of liquid product/grams of materials (ethylene+hydrogen chloride) used) × 100. b) The yields of each compound produced were given by (grams of each compound/grams of total reaction product) × 100.

Table 3. Influence of the discharge time on the yield of reaction products (Experimental conditions)

Experiment No.	13	14	15	16[a]	17[a]
Materials used (l)					
Ethylene	4.60	4.88	4.90	6.30	5.73
Hydrogen chloride	9.07	8.90	8.79	7.37	8.03
Molar ratio (C_2H_4/HCl)	0.53	0.55	0.56	0.85	0.72
Discharge time (h)	4	2	1	8	4
Temp. of discharge tube (°C)					
Inside	25—48	25—47	25—47	25—45	25—47
Outside	25	25	25	25	25
Second voltage (KV)	15	15	15	15	15
Second current (mA)	2.8	2.5	2.4	2.8	2.5

a) Experiment Nos. 16 and 17 show the results when the products coming out of the discharge tube were collected by being passed through two traps cooled at −70 °C by acetone–Dry Ice.

chlorohexane seem to be formed by the telomerization between ethylene and hydrogen chloride. The formation of 1-chlorooctane (1 : 4 telomer) and one-to-five or more products could not be observed by gas chromatographic analysis.

Influence of the Discharge Temperature. The discharge reactions were performed at 5, 25, 50, and 75 °C, as shown in Table 1. As may be seen from the results of these experiments shown in Table 2, the conversion efficiency [grams of liquid product/grams of materials (ethylene+hydrogen chloride) used×100] depends upon the temperature at which the discharge is carried out; when the molar ratio of the reactants was about 1: 1, the maximum yield of the liquid products was obtained at 25 °C, the proportions of 1-chlorobutane and 1,4-dichlorobutane in the liquid product decreased with increasing temperature, and the gaseous products increased with the rise in the discharge temperature and the increase in the ethylene concentration. It may be said that the telomer formation with $n=2$ is favored by a low temperature.

Influence of the Discharge Time. The discharge reaction was carried out with various reaction times (1, 2, 4, and 8 h), as is shown in Table 3; the results are summarized in Table 4. The total pressure in the reaction system was measured at intervals of 30 min. The results shown in Fig. 2 and Table 4 show that lowering the total pressure increases the amount of the

Table 4. Influence of the discharge time on the yield of reaction products (Experimental results)

Experiment No.	13	14	15	16	17
Liquid product collected (g)	9.90	5.30	2.34	10.77	10.74
Conversion efficiency (%)	48.2	25.7	11.4	54.2	53.1
Composition of liquid reaction products (%)					
Chloroethylene	0.5	0.9	1.0	0.2	1.4
Chloroethane	66.7	70.9	72.7	61.5	73.0
1-Chlorobutane	5.1	4.6	4.2	7.1	4.5
2-Chlorobutane	1.9	1.2	0.7	2.0	1.4
1,4-Dichlorobutane	13.9	13.4	12.9	12.8	10.9
1,3-Dichlorobutane	3.0	2.5	1.5	4.4	2.1
2,3-Dichlorobutane	1.3	0.6	0.4	2.4	0.6
1,2-Dichlorobutane	1.0	0.3	T	2.3	0.1
1-Chlorohexane	0.3	0.2	0.2	0.8	0.1
1,1-Dichloroethane	0.7	0.4	0.3	1.4	0.4
1,2-Dichloroethane	2.2	1.8	1.7	2.6	1.7
1,2,4-Trichlorobutane	0.9	0	0	T	0
1-Chloropropane	0.4	0.2	0.2	0.5	0.3
2-Chloropropane	0.4	T	T	0.1	T
1,2-Dichloropropane	0.4	0.1	T	0.2	0.2
1,3-Dichloropropane	0.6	0.1	0.1	0.8	0.3
1-Butene	0.1	0.2	0.2	T	0.3
Butane	0.1	0.2	0.2	T	0.4
1,3-Butadiene	0.1	0.2	0.2	T	0.3
Unidentified products	0.4	2.2	3.5	0.9	2.0

Table 5. The reactions of ethylene with chloro compounds in silent electrical discharge (Experimental conditions)

Experiment No.	18a)	19a)	20b)	21b	22
Materials used (l)					
Ethylene	—	4.14	—	4.42	6.66
Chloroethane	5.29	4.73	—	—	—
Chloroethylene	—	—	4.61	4.74	—
Hydrogen chloride	8.48	4.66	9.21	4.69	—
Chlorine	—	—	—	—	7.16
Temp. of discharge tube (°C)					
Inside	25—41	25—40	25—45	25—45	25—40
Outside	25	25	25	25	25
Discharge time (h)	8	8	8	8	3
Second voltage (kV)	15	15	15	15	15
Second current (mA)	2.1	2.3	2.2	2.2	2.8

a) Experiment Nos. 18 and 19 show the results when the products were collected by two traps cooled at 10 °C. b) The products were collected by being passed through two traps cooled at -10 °C by acetone–Dry Ice.

liquid product. The yield of the reaction products and the velocity of the reduced pressure in the reaction system increased rapidly until 4 h of reaction time, while beyond this, they increased only gradually. Chloroethane in the reaction products decreased with the progress of the discharge time. As may be seen from Experiment No. 4 of Table 2 and Experiment No. 16 of Table 4, when the reaction product coming out of the discharge tube was cooled at -70 °C by acetone–Dry Ice, the conversion efficiency and the yield of chloroethane increased. When the reaction product coming out of the discharge tube was cooled at -50 °C, the yields of telomer with $n=2$ and dichloro compounds of butane increased. These results suggest that the noncondensable chloroethane is concerned in the secondary process.

The Reaction of Ethylene with Chloro Compounds

The mixture of ethylene and several chloro compounds, such as chloroethane, chloroethylene, hydrogen chloride, and chlorine was discharged in an ozonizer under the reaction conditions shown in Table 5; the results are summarized in Table 6. In the reaction of ethylene and chlorine, the main product was 1,2-dichloroethane. This suggests that the addition reaction occurs predominantly on account of the high reactivity of chlorine. As can be seen from Experiment Nos. 18 and 19 in Tables 5 and 6, when the mixtures of chloroethane and hydrogen chloride or of both compounds and ethylene

Table 6. The reactions of ethylene with chloro compounds in silent electrical discharge (Experimental results)

Experiment No.	18	19	20	21	22
Liquid product collected (g)	7.73	4.40	20.69	8.89	24.70
Composition of liquid reaction products (%)					
Chloroethylene	T	0.2	1.7	8.2	T
Chloroethane	11.9	23.3	1.6	5.1	1.0
1-Chlorobutane	1.0	9.3	0.4	9.3	0.4
2-Chlorobutane	0.7	3.1	0.2	2.9	0.2
1,4-Dichlorobutane	17.8	27.2	1.9	11.8	0.6
1,3-Dichlorobutane	20.7	19.3	3.3	13.6	0
2,3-Dichlorobutane	15.2	5.7	3.1	7.1	0
1,2-Dichlorobutane	14.1	3.8	3.1	2.1	0
1-Chlorohexane	T	1.3	T	1.5	0
1,1-Dichloroethane	0.9	0.6	0.9	1.4	0.4
1,2-Dichloroethane	1.7	1.5	8.4	5.9	92.8
1,2,4-Trichlorobutane	11.5	1.2	53.2	24.2	0
1-Chloropropane	0.1	0.7	0	0.6	0
2-Chloropropane	0.3	0.1	0	0.1	0
1,2-Dichloropropane	1.2	0.4	T	0.4	0
1,3-Dichloropropane	1.6	1.1	T	0.9	0
1-Butene	T	0.1	0.1	T	T
Butane	T	0.1	T	T	T
1,3-Butadiene	T	0.1	T	T	T
Unidentified products	1.3	1.9	22.1	4.9	4.6

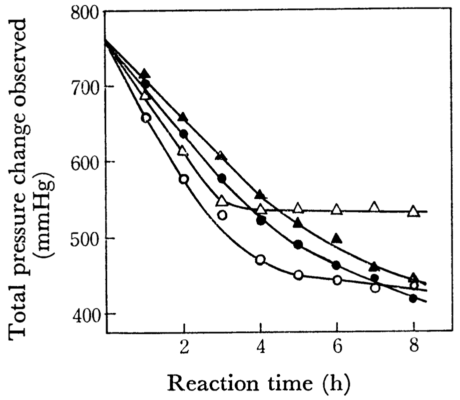

Fig. 2. Relation between total pressure in reaction system and time of reaction.
Experiment No., ▲: No. 2, △: No. 4, ●: No. 5, ○: No. 11.

were discharged, they were mainly transformed into the dichloro compounds of butane. Similar experiments (Nos. 20 and 21) with chloroethylene showed formation of considerable amounts of the trichloro compound (1,2,4-trichlorobutane) and the dichloro compounds of butane. When a mixture of ethylene and hydrogen chloride was discharged in an ozonizer a small amount of chloroethylene in the liquid products was obtained. This suggests that the chloroethylene may be formed by the primary process, but will be rapidly involved in the secondary process owing to its great activity.

The Mechanism of the Formation of the Main Products Obtained by the Reaction of Ethylene and Hydrogen Chloride. The molecules excited by the silent discharge are considered to change into radicals or atoms, and into small amounts of ionized molecules as has been reported by many workers.[9] Accordingly, the reaction of ethylene with hydrogen chloride in a silent electrical discharge is guessed to be a vapor-phase radical reaction. Egloff *et al.*[10] reported that a vinyl radical was formed from ethylene in the electrical discharge, and that it was produced by breaking a carbon-hydrogen bond. Tsutsumi[11] reported that the vinyl radical was produced by two molecular processes,[12] as is shown below. Franklin *et al.*[13] reported the formation of activated monochloroethyl radicals in the photochlorination of ethylene. Golden and Ausloos[14] reported that the vacuum-ultraviolet photolysis of ethylene led essentially to three types of processes, as is indicated below.[15]

The mechanism of the formation of chloroethane, 1-chlorobutane, and 1-chlorohexane by the reaction of ethylene with hydrogen chloride may be represented as follows: The first step is the activation of the ethylene molecule and the hydrogen chloride molecule by electron impact, 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,[12] and (2) the decomposition of the activated molecules to give the vinyl radical, the chlorine radical, and the hydrogen atom. Chloroethane may be formed by four paths: (1) the combination of the ethyl radical and the chlorine radical; (2) the reaction of the chlorine radical with ethylene, and the reaction between hydrogen chloride and the monochloroethyl radical so formed; (3) the addition of hydrogen atom to the monochloroethyl radical produced by (2); and (4) the formation of chloroethylene by the combination of the vinyl radical and chlorine radical, and then the addition of hydrogen atoms to the chloroethylene thus obtained. The formation of acetylene, 1,3-butadiene, and 1-butene may show the existence of the vinyl radical. And the formation of ethane, butane, and 1-butene may indicate the production of the ethyl radical. Since chloroethylene as described above has high activity in the presence of hydrogen chloride and ethylene under a silent discharge, it is changed into the dichloro compounds and the trichloro compound (1,2,4-trichlorobutane) of butane. The formation of 1-chlorobutane and 1-chlorohexane may be represented as follows:

$$CH_2{=}CH_2 + \cdot Cl \longrightarrow \dot{C}H_2CH_2Cl$$

$$\dot{C}H_2CH_2Cl + CH_2{=}CH_2 \longrightarrow \dot{C}H_2(CH_2)_3Cl$$

$$\dot{C}H_2(CH_2)_3Cl + HCl \longrightarrow CH_3(CH_2)_3Cl + \cdot Cl$$

$$\dot{C}H_2(CH_2)_3Cl + CH_2{=}CH_2 \longrightarrow \dot{C}H_2(CH_2)_5Cl$$

$$\dot{C}H_2(CH_2)_5Cl + HCl \longrightarrow CH_3(CH_2)_5Cl + \cdot Cl$$

The mechanism mentioned above is the telomerization reaction in which hydrogen chloride acts as the telogen. The addition reaction of the $\cdot CH_2(CH_2)_5Cl$ radical to ethylene in these reaction mechanisms need not be considered, since no products beyond 1-chlorooctane (1: 4 telomer) were obtained. Compared with the yield of 1-chlorobutane (1: 2 telomer), the yield of 1-chlorohexane (1: 3 telomer) decreased remarkably. Therefore, it is considered that the unpaired electron of the end CH_2 and the Cl atom in the $CH_2(CH_2)_3Cl$ radical form a pseudo cyclic arrangement.* On the other hand, the formation of 1,4-dichlorobutane may proceed by two paths: (1) the reaction between $\cdot CH_2(CH_2)_3Cl$ radical and hydrogen chloride or chlorine radical, (2) the coupling reaction between two $\cdot CH_2CH_2Cl$ radicals. Other dichloro compounds of butane may be formed by various secondary processes. The formation of 2-chlorobutane was also observed. 2-Chlorobutane may be formed by two paths: (1) the isomerization of 1-chlorobutane, and (2) the reaction between hydrogen chloride or ethylene and chloroethylene, the addition of CH_3–$\dot{C}HCl$ radical thus obtained to ethylene, and then the reaction of the CH_3CHCl–CH_2–$\dot{C}H_2$ radical and hydrogen chloride.

The Reactions between HX, such as Hydrogen Cyanide, Hydrogen Sulfide, and Hydrogen Chloride, and Ethylene. The reactions of ethylene with hydrogen cyanide or hydrogen sulfide in the silent electrical discharge were carried out.[3] The results obtained are summarized in Table 7. In the case of the reaction between ethylene and hydrogen cyanide, the main product was acrylonitrile. Besides this compound, ethyl cyanide, butyl cyanide, and *s*-butyl cyanide *etc.* were obtained. No compound combined with two CN groups was obtained. In the case of the reaction between ethylene and hydrogen sulfide, the main product was ethanethiol. However, the product (1,2-ethanedithiol) combined with two SH groups was formed. As may be seen from Tables 2 and 7, when hydrogen chloride, hydrogen sulfide, and hydrogen cyanide as reactants (HX) were used, the yields of the liquid products decrease in the following order: HCl>H_2S>HCN. When the hydrogen chloride was used, the yield of liquid product was especially remarkable.

TABLE 7. THE REACTIONS BETWEEN ETHYLENE AND HYDROGEN SULFIDE OR HYDROGEN CYANIDE IN SILENT ELECTRICAL DISCHARGE

Experiment No.	23[a]	24[b]
Materials used (l)		
Ethylene	19.6	27.6
Hydrogen sulfide	29.4	—
Hydrogen cyanide	—	44.8
Molar ratio (C_2H_4/HX)[c]	0.7	0.6
Second voltage (kV)	12	15
Second current (mA)	2.1	2.1
Discharge time (h)	6	9
Discharge temp. (°C)		
Inside	19—49	10—26
Outside	19—41	10
Liquid product collected (g)	7.00	6.47
Composition of liquid reaction products (%)		
$CH_2{=}CHX$	0	45.9
CH_3CH_2X	61.6	12.9
$CH_3CH_2CH_2CH_2X$	3.5	17.1
$CH_3CH_2CHXCH_3$	0.1	10.2
$CH_3(CH_2)_4CH_2X$	T	T
XCH_2CH_2X	24.2	0

a) The discharge tube used was a Pyrex tube of the Siemens type with a space gap of 2.5 mm and an effective length of 45 cm. b) This experiment was performed by using the flow system. c) X: SH or CN radicals.

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* Beer and Besprozvannyi[16] found, from their data on the telomerization of ethylene in carbon tetrachloride and chloroform, that compounds ($ClCH_2(CH_2)_3CCl_3$ and $CH_3(CH_2)_3$-CCl_3) with $n=2$ were formed over a wide range of ethylene concentration. They suggested that the predominance of telomers with $n=2$ resulted from the stabilization of the trichloroamyl radical by a "pseudo cyclic" configuration between the unpaired electron of the end CH_2 and the electrophilic CCl_3 groups.

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