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Effect of Hydrogen Chloride on the Pyrolysis of Acetylene as Studied with a Single-pulse Shock Tube

Hiroo OGURA

Institute of Space and Aeronautical Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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The pyrolysis of acetylene in the presence of hydrogen chloride was investigated with a single-pulse shock tube in the temperature range 1100—1680 K. The hydrocarbons produced in the C_2H_2–HCl system were quite the same as those obtained in the C_2H_2–Ar system. The formation rate of the main pyrolysis product, 1-buten-3-yne, was reduced remarkably by the addition of hydrogen chloride, being of third-order and of inverse first-order with respect to the concentrations of acetylene and hydrogen chloride, respectively. The overall second-order rate constant obtained was

$$k(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 2.9\times10^{12}\exp(-45800/RT).$$

As the chlorine atom containing product, only chloroacetylene was found in small amounts, its formation rate being of second-order with respect to acetylene. The inhibitory effect of hydrogen chloride on the 1-buten-3-yne formation rate was interpreted in terms of the change in the termination from the recombination reaction of 2-ethynylvinyl radical to the reaction of 2-ethynylvinyl radical with hydrogen chloride.

Hydrogen chloride has been used as an additive that may scavenge the chain carrier radicals in the system of decomposing hydrocarbons. Cullis *et al.*[1]) studied the pyrolysis of acetylene in the presnece of hydrogen chloride at temperatures below 800 K, reporting that it may inhibit the pyrolysis of acetylene by a different mechanism from that of nitrogen monoxide. On the other hand, using a shock tube Bopp and Kern found that hydrogen chloride has no appreciable effect on the pyrolysis of acetylene at temperatures above 1650 K.[2])

A shock tube study on the pyrolysis of acetylene in the presence of nitrogen monoxide at intermediate temperatures showed that the nitrogen monoxide ceases to be an inhibitor with rise in temperature.[3]) Analyses of both the yield-temperature plots of the pyrolysis products and the reaction products containing chlorine atom would be useful for a mechanistic study of the inhibitory effect of hydrogen chloride, as was found in the case of the C_2H_2–NO system.

Experimental

Apparatus and Procedure. The apparatus and procedure were the same as those described previously.[3]) A 4-cm single-pulse shock tube was used, the driven section being 277 cm and the driver section 128.5 cm in length. Helium was used as a driver gas. The shocks were fired within 5 min after the test gases had been introduced into the driven section.

Materials. Four mixtures were prepared in a glass vessel of 10-l volume with the ratios of C_2H_2/HCl/Ar = 10/2/88; 10/0.5/89.5; 5/1/94; and 10/0/90. The test mixtures were stirred with a glass fan for 4 h. The mixing and storage time periods were kept constant for the three mixtures with hydrogen chloride, since too long storage resulted in the formation of vinyl chloride in a considerable amount. One mixture completely mixed was shock-heated within 2 d, the vinyl chloride formation being negligible.

Hydrogen chloride (Matheson Co.) was purified by bulb-to-bulb distillation. Argon and acetylene were purified according to the method reported.[3]) The standard gas mixtures for the calibration of gas-chromatography were the same as those used previously.[3])

Chloroacetylene was synthesized from 1,2-dichloroethylene by the method of Bashford *et al.*[4]) The chloroacetylene was purified by bulb-to-bulb distillation. The gas-chromatographic and mass spectrometric analyses showed that no detectable impurities were found. The purified chloroacetylene was diluted with a large amount of argon, and used as a gas-chromatographic standard gas.

Analytical. The reaction products were analyzed by gas-chromatography. The details of the hydrocarbon analysis were described elsewhere.[3]) Chloroacetylene and vinyl chloride were analyzed in the same way as the hydrocarbons on a Porapak N column at 140 °C. The order of elution was CH_4, C_2H_6, C_2H_4, allene, propyne, chloroacetylene, vinyl chloride, 1,3-butadiene, 1-buten-3-yne, 1,3-butadiyne, and benzene. Hydrogen was analyzed at room temperature with a thermal conductivity cell on a 1.2 m column packed with molecular sieve 13X(80—100 mesh), argon being used as a carrier gas.

Results

The mixtures were subjected to shock-heating in the temperature range 1100—1680 K. The total densities behind the reflected shock waves were *ca.* 2.68×10^{-5} mol/cm^3, the reaction times being *ca.* 990 μs. The shock-heated samples were extracted into pre-evacuated bulbs of 60-ml volume, and analyzed by gas-chromatography.

Product analysis showed that the hydrocarbons produced with and without hydrogen chloride were the same; CH_4, C_2H_4, C_2H_6, allene, propyne, 1,3-butadiene, 1-buten-3-yne, 1,3-butadiyne, and benzene being formed. The major products were also 1-buten-3-yne, 1,3-butadiyne, and hydrogen in the presence of hydrogen chloride. The minor products were CH_4, C_2H_4, allene, propyne, and benzene, trace products being C_2H_6 and 1,3-butadiene as in the case of acetylene.

Chloroacetylene was produced in a small amount as a product containing chlorine atom. The chloroacetylene was identified by both gas-chromatographic and mass spectrometric comparison with the synthesized gas. Substances condensible at liquid nitrogen temperature in several runs at higher reaction temperatures were used for identification. No products which might contain chlorine atoms were detected in the substances condensible at liquid nitrogen temperature.

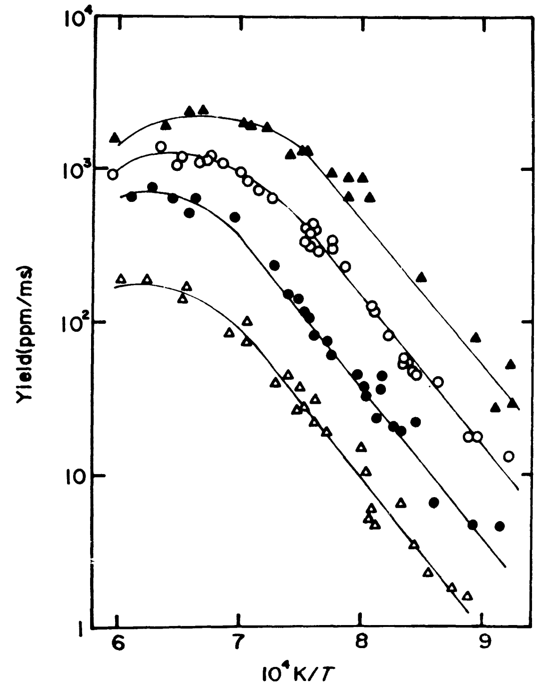

Fig. 1. Yield-temperature plots of 1-buten-3-yne formation.
●; $C_2H_2/HCl/Ar = 10/2/88$, ○; $C_2H_2/HCl/Ar = 10/0.5/89.5$, △; $C_2H_2/HCl/Ar = 5/1/94$, ▲; $C_2H_2/HCl/Ar = 10/0/90$.

Inhibited Rate of 1-Buten-3-yne Formation. The yields of 1-buten-3-yne(ppm/ms) for four mixtures with different composition of C_2H_2 and HCl are plotted as a function of temperature in Fig. 1. The yield-temperature plots show that the yields of 1-buten-3-yne are markedly decreased by the addition of hydrogen chloride at lower temperatures, and that they are significantly dependent on the amount of hydrogen chloride added. The rates of 1-buten-3-yne formation at temperatures below 1350 K are nearly of third order with respect to acetylene and of inverse first order with respect to hydrogen chloride. Apparent overall second-order rate constants for the inhibited 1-buten-3-yne formation at temperatures below 1350 K (58 experiments) are plotted in the Arrhenius form in Fig. 2. The best fit rate constant expression was obtained by the least-squares method as[5]

$$k_1(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 2.9 \times 10^{12} \exp(-45800/RT)^* . \quad (1)$$

Formation Rate of Chloroacetylene. The formation of chloroacetylene was expected to have something to do with the reduction of 1-buten-3-yne yields. In order to determine the concentration dependence of the rate of chloroacetylene formation on acetylene and hydrogen chloride, the yields of chloroacetylene are plotted as a function of temperature in Fig. 3. We see that the rates of chloroacetylene formation are approximately of second-order with respect to acetylene and are little dependent on the hydrogen chloride concentration. Apparent second-order rate constants of 43 experiments are shown in the Arrhenius form in Fig. 4. The least-squares treatment of the data gives the best fit rate constant as[5]

$$k_2(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 1.0 \times 10^{16} \exp(-67200/RT) . \quad (2)$$

Only the data obtained at temperatures below 1350 K were adopted, since the yields of chloroacetylene decreased at higher temperatures and the temperatures where the yields began to decrease differed for the three mixtures with hydrogen chloride.

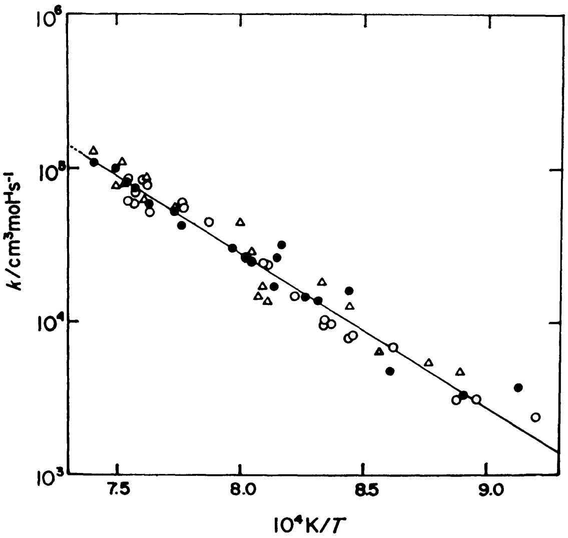

Fig. 2. Arrhenius plots of the second-order rate constants for 1-buten-3-yne formation.
Symbols are the same as in Fig. 1.

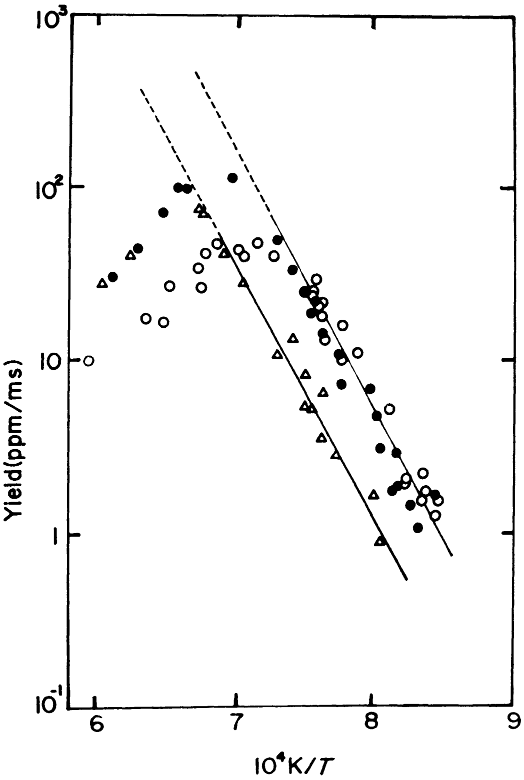

Fig. 3. Yield-temperature plots of chloroacetylene formation.
Symbols are the same as in Fig. 1.

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* The activation energy is expressed in cal/mol (1 $\mathrm{cal_{th}} =$ 4.184 J).

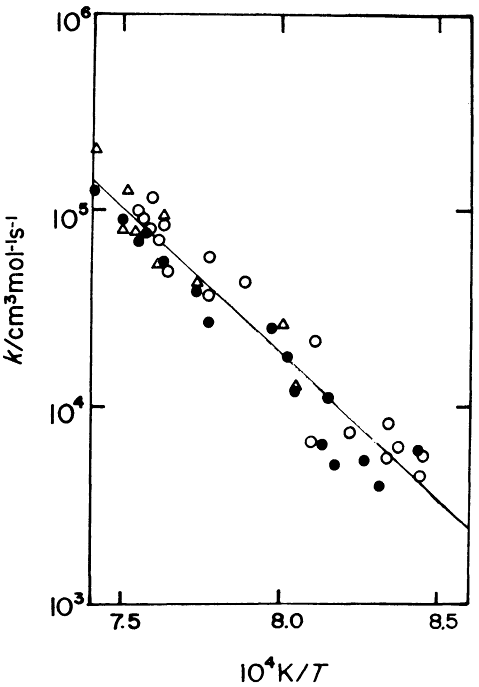

Fig. 4. Arrhenius plots of the second-order rate constants for chloroacetylene formation.
Symbols are the same as in Fig. 1.

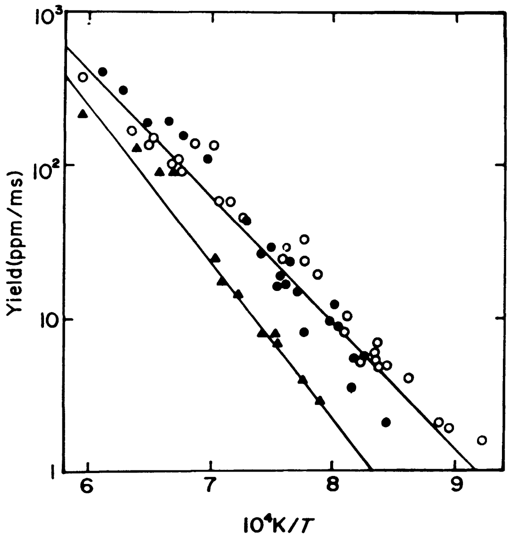

Fig. 5. Effect of hydrogen chloride on the yields of ethylene. Symbols are the same as in Fig. 1.

Effects on Other Products. Hydrogen chloride affects the yields of other products in two different ways: (a) in the case of 1,3-butadiyne, hydrogen, and ethylene, the yields increase considerably at lower temperatures, and at higher temperatures are little influenced by the concentration of hydrogen chloride added (Fig. 5); (b) in the case of allene, propyne, and benzene, the yields decrease significantly at lower temperatures, the decrease becoming smaller with rise in temperature.

Discussion

The hydrocarbons produced in the C_2H_2–HCl system are the same as those in the pyrolysis of acetylene. Although their yields are affected by the addition of hydrogen chloride, the forms of yield-temperature plots are similar to those in the absence of hydrogen chloride. This suggests that a mechanism similar to that of the pyrolysis alone is operative in the C_2H_2–HCl system. A pyrolysis mechanism for acetylene has been proposed from a thermochemical point of view,[6] and tested by the addition of nitrogen monoxide.[3] The mechanism is as follows:

$$\begin{array}{lll}
2C_2H_2 \longrightarrow C_4H_3(1) + H & \Delta H^\circ = 46.2 & (3)\\
C_4H_3(1) + C_2H_2 \longrightarrow C_6H_5 & \Delta H^\circ = -20.5 & (4)\\
C_6H_5 \longrightarrow C_4H_4 + C_2H & \Delta H^\circ = 53.1 & (5)\\
C_2H + C_2H_2 \longrightarrow C_4H_3(2) & \Delta H^\circ = -44.8 & (6)\\
C_4H_3(2) + C_2H_2 \longrightarrow C_4H_4 + C_2H & \Delta H^\circ = 11.7 & (7)\\
2C_4H_3(2) \longrightarrow \text{termination} & & (8)
\end{array}$$

C_4H_3 (1) and C_4H_3 (2) stand for 1-ethynylvinyl and 2-ethynylvinyl radicals, respectively.

Inhibitory Effect of Hydrogen Chloride. A free-radical chain mechanism for the inhibited formation of 1-buten-3-yne could be constructed in line with that for the pyrolysis of acetylene. The inhibitory effect of hydrogen chloride can be interpreted by the reactions with the radicals present in the pyrolysis system of acetylene alone:[7]

$$\begin{array}{lll}
C_4H_3(1) + HCl \longrightarrow C_4H_4 + Cl & \Delta H^\circ = 23.8 & (9')\\
\qquad\qquad \longrightarrow C_4H_3(1)Cl + H & & (9'')\\
C_2H + HCl \longrightarrow C_2H_2 + Cl & \Delta H^\circ = -8.8 & (10')\\
\qquad\qquad \longrightarrow C_2HCl + H & \Delta H^\circ = 11.3 & (10'')\\
C_4H_3(2) + HCl \longrightarrow C_4H_4 + Cl & \Delta H^\circ = 2.0 & (11')\\
\qquad\qquad \longrightarrow C_4H_3(2)Cl + H & & \\
 & \Delta H^\circ = 19.8 & (11'')
\end{array}$$

The reaction of C_6H_5 radical with HCl can be neglected, since the bimolecular reaction would be too slow to be competitive with the unimolecular decomposition of C_6H_5 radical (Reaction 5). The mechanism for the inhibited pyrolysis consists of three sets of competitive reactions of the radicals with C_2H_2 and HCl. The reaction of C_4H_3 (1) radical with HCl (Reactions 9′ and 9″) is referred to hereafter as Reaction 9.

The characteristic feature of the 1-buten-3-yne formation rates in the C_2H_2–HCl system is their concentration dependence on C_2H_2 and HCl. The formation rates are inversely proportional to the concentration of HCl. The inverse first-order dependence on an additive is observed when the termination reaction in its absence is replaced by a reaction of the predominant radical with the additive.[8] Thus Reaction 8, the major termination in the reaction C_2H_2–Ar system, would become a minor one in the C_2H_2–HCl system.

Assuming the steady-state concentrations of C_4H_3 (1), C_2H, C_6H_5, and C_4H_3 (2) radicals in Reactions 3—11, we get

$$R_3 = 2R_8^{\mathrm{HCl}} + R_9 + R_{10} + R_{11}. \qquad (12)$$

Since the contribution of Reaction 8 to the termination would be small, $2R_8^{\mathrm{HCl}}$, R_8^{HCl} denoting the rate of Reaction 8 in the presence of HCl, can be neglected:

$$R_3 \simeq R_9 + R_{10} + R_{11}. \qquad (12')$$

In the absence of hydrogen chloride, the steady-state concentrations of the radicals are expressed as follows:

$$[C_4H_3(1)]_{ss} = (k_3/k_4)[C_2H_2] \tag{13}$$

$$= 56\exp(-40900/RT)[C_2H_2] \tag{13'}$$

$$[C_2H]_{ss} = [C_4H_3(1)]_{ss} + (k_7/k_6)[C_4H_3(2)]_{ss} \tag{14}$$

$$\simeq 3.8\times10^2\exp(-30900/RT)[C_2H_2] \tag{14'}$$

$$[C_4H_3(2)]_{ss} = (k_3/2k_8)^{1/2}[C_2H_2] \tag{15}$$

$$= 3.0\exp(-23700/RT)[C_2H_2] \tag{15'}$$

The rate constants used in the above estimation are those adopted previously:[3]

$$k_3(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 3.5\times10^{13}\exp(-47400/RT) \tag{16}$$

$$k_6(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 6.5\times10^{11}\exp(-6500/RT) \simeq k_4 \tag{17}$$

$$k_7(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 7.9\times10^{13}\exp(-22600/RT) \tag{18}$$

$$k_8(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 2.0\times10^{12}. \tag{19}$$

From Eqs. 13′, 14′, and 15′, C_4H_3 (1) and C_4H_3 (2) are found to be the least and most abundant radicals in the C_2H_2–Ar system, respectively.

Although the change of concentration dependence of 1-buten-3-yne formation rate upon the addition of HCl might indicate that the hydrogen chloride added decreases the steady-state concentrations of the radicals in the C_2H_2–HCl system considerably, the C_4H_3 (2) radical would be the most predominant chain carrier radical even in the C_2H_2–HCl system. Neglecting the contribution of Reactions 9 and 10 to the termination, Eq. 12′ can be approximated by

$$R_3 = k_3[C_2H_2]^2 \simeq k_{11}[C_4H_3(2)]_{ss}^{HCl} = R_{11} \tag{12''}$$

from which we get the steady-state concentration of $C_4H_3(2)$ in the presence of HCl, $[C_4H_3(2)]_{ss}^{HCl}$:

$$[C_4H_3(2)]_{ss}^{HCl} \simeq (k_3/k_{11})[C_2H_2]^2/[HCl] \tag{20}$$

In the present mechanism 1-buten-3-yne is formed mainly by Reaction 7.

$$R_{C_4H_4}^{HCl} \simeq R_7^{HCl} \simeq k_7(k_4/k_{11})[C_2H_2]^3/[HCl], \tag{21}$$

where the formation rate of 1-buten-3-yne in the presence of HCl is denoted by $R_{C_4H_4}^{HCl}$. The formation rate derived from the present mechanism is in line with the observed one as regards concentration dependence.

Since no rate constants, estimated or observed, are available, k_{11} is calculated by a comparison with the observed (Eq. 1) and estimated (Eq. 21) rates for 1-buten-3-yne formation to be

$$k_{11}(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) \simeq k_3k_7/k_1, \tag{22}$$

$$= 9.5\times10^{14}\exp(-24200/RT). \tag{22'}$$

The rate constant estimated in Eq. 22′ is a representative one for both Reactions 11′ and 11″, its activation energy being greater than their heats of reaction. In view of the heat of reaction, the activation energy of Reaction 11″ is expected to be greater than that of Reaction 11′. When the activation energy of k_{11} is attributed to Reaction 11″, the activation energy for the inverse Reaction 11″ is estimated to be 4.4 kcal/mol from the heat of reaction. In the case of CH_3 radical reactions with HCl, the activation energies for the inverse reactions are obtained experimentally to be 4.6 kcal/mol for $H+CH_3Cl$ and 2.5 kcal/mol for $Cl+CH_4$.[9–11]

No detectable amount of chlorine atom containing products except for C_2HCl was found. $C_4H_3(2)Cl$ would undergo a unimolecular decomposition at temperatures above 1100 K as in the case of C_2H_3Cl.[12]

$$C_4H_3(2)Cl \longrightarrow C_4H_2 + HCl \qquad \Delta H^\circ = 20.4 \tag{23}$$

By this reaction the yields of C_4H_2 should increase upon addition of HCl, this being in line with the experimental results, In the present free-radical mechanism HCl catalizes the decomposition of the $C_4H_3(2)$ radical at temperatures above 1100 K.

The formation rate of 1-buten-3-yne in the absence of HCl has been reported:[6]

$$R_{C_4H_4} = 2.4\times10^{14}\exp(-46400/RT)[C_2H_2]^2. \tag{24}$$

In the present mechanism the steady-state concentrations of the $C_4H_3(2)$ radical with and without HCl are related to the observed 1-buten-3-yne formation rates as follows:

$$[C_4H_3(2)]_{ss}^{HCl}/[C_4H_3(2)]_{ss} = R_7^{HCl}/R_7 = R_{C_4H_4}^{HCl}/R_{C_4H_4} \tag{25}$$

$$= 1.2\times10^{-2}\exp(600/RT)[C_2H_2]/[HCl]. \tag{25'}$$

In the presence of HCl the steady-state concentration of $C_4H_3(2)$ radical is reduced by a factor 0.1—0.3 of that in its absence (1100—1350 K and $[C_2H_2]/[HCl]=5$—20). The chain length of 1-buten-3-yne formation rate in the C_2H_2–Ar system is given by

$$R_{C_4H_4}/R_3 = R_{C_4H_4}/R_8 = 7.1\exp(1000/RT), \tag{26}$$

$$\simeq 10(1100\text{—}1350\,\mathrm{K}). \tag{26'}$$

The chain length in the C_2H_2–HCl system is shortened to *ca.* 1—3 under the present experimental conditions, since the 1-buten-3-yne formation rate is proportional to the steady-state concentration of C_4H_3 (2) radical. In the system with the composition of $[C_2H_2]/[HCl]=5$, the chain length is *ca.* 1.0 at temperatures 1100—1350 K, the chain being almost completely stopped.

The contribution of Reaction 8 to the termination in the C_2H_2–HCl system is estimated by means of Eqs. 12″ and 25.

$$R_8^{HCl} \simeq (1/10\text{—}1/100)R_8 \simeq (1/10\text{—}1/100)R_{11}.$$

As assumed in the derivation of Eq. 12″, Reaction 8 in the C_2H_2–HCl system is found to be an insignificant termination.

Formation Rate of Chloroacetylene. The steady-state approximation made in the derivation of Eq. 12 also gives the equation

$$R_6^{HCl} = R_7^{HCl} + R_{11} \tag{27}$$

from which the steady-state concentration of C_2H radical is obtained as

$$[C_2H]_{ss}^{HCl} = (1/k_6)(k_7+k_{11}[HCl]/[C_2H_2])[C_4H_3(2)]_{ss}^{HCl}. \tag{28}$$

In the present mechanism the chloroacetylene is formed by Reaction 10″. The formation rate is then expressed by

$$R_{C_2HCl} = (k_3k_{10''}/k_6k_{11})(k_7[C_2H_2]^2 + k_{11}[C_2H_2[HCl]), \tag{29}$$

$$= (k_3k_7/k_6)(k_{10''}/k_{11})[C_2H_2]^2(1+R_{11}/R_7^{HCl}). \tag{29'}$$

Since the formation rate of chloroacetylene is little dependent on the hydrogen chloride concentration in the present experiments, to be compatible with the observed rate, Eq. 29′ can be approximated by

$$R_{C_2HCl} \simeq (k_3k_7/k_6)(k_{10''}/k_{11})[C_2H_2]^2. \qquad (29'')$$

By a comparison of the estimated second-order rate constant with the observed one (Eq. 2), we obtain

$$k_{10''}/k_{11} = 2.3\exp(-3700/RT), \qquad (30)$$

$$\simeq 0.4\text{—}0.6\,(1100\text{—}1350\,\mathrm{K}). \qquad (30')$$

The rate constant k_{10}'' is then obtained from Eqs. 22′ and 30:

$$k_{10''}(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 2.2\times10^{15}\exp(-27900/RT) \qquad (31)$$

The frequency factors of k_{10}'' and k_{11} seem to be somewhat greater than that of the usual abstraction reaction, *i.e.*, 10^{13}—10^{14}. However, they might be reasonable as considered from the assumptions made in their derivation. The effective rate constants for Reactions 10 and 11 might be of comparable order of magnitude, since these reactions are of a similar type. This may be supported by Eq. 30′.

Using the estimated rate constants k_{10}'' and k_{11}' we can evaluate the relative importance of the competitive reactions of the radicals with C_2H_2 and HCl. The contribution of k_{10}' to k_{10} can be neglected in analogy with Reaction 11.

$$R_{10}/R_6^{HCl} \simeq (k_{10''}/k_6)[HCl]/[C_2H_2],$$

$$= 3.4\times10^3\exp(-21400/RT)[HCl]/[C_2H_2],$$

$$R_{11}/R_7^{HCl} = (k_{11}/k_7)[HCl]/[C_2H_2],$$

$$= 12\exp(-1600/RT)[HCl]/[C_2H_2],$$

$$(R_{10}/R_6^{HCl})/(R_{11}/R_7^{HCl}) \simeq (k_7/k_6)(k_{10''}/k_{11}),$$

$$= 3.0\times10^2\exp(-19800/RT),$$

$$\simeq 0.04\text{—}0.2\,(1100\text{—}1350\,\mathrm{K}).$$

The equations show that the scavenging of C_2H radical by HCl molecule is less important than that of $C_4H_3(2)$ radical. This is in line with the assumption made in the derivation of 1-buten-3-yne formation rate.

Reactions of Other Radicals. In the absence of HCl, C_2H_4 is formed by the following reaction.[6]

$$H + C_2H_2 \longrightarrow C_2H_3, \qquad \Delta H^\circ = -46.7 \qquad (32)$$

$$C_2H_3 + C_2H_2 \longrightarrow C_2H_4 + C_2H, \qquad \Delta H^\circ = 12.7. \qquad (33)$$

In the presence of HCl, the C_2H_3 radical will react with HCl.

$$C_2H_3 + HCl \longrightarrow C_2H_4 + Cl, \qquad \Delta H^\circ = 3.9 \qquad (34')$$

$$\longrightarrow C_2H_3Cl + H, \qquad \Delta H^\circ = 19.6 \qquad (34'')$$

$$C_2H_3Cl \longrightarrow C_2H_2 + HCl. \qquad \Delta H^\circ = 27.1 \qquad (35)$$

As in the case of Reaction 11, the activation energy of Reaction 34′ would be smaller than that of Reaction 34″. In view of the heat of reaction the activation energy of Reaction 34′ would be smaller than that of Reaction 33, the yields of C_2H_4 thus increasing with the reaction of HCl at lower temperatures.

The C_2H_3 radical becomes a radical of greater molecular weight by successive reactions with C_2H_2 molecules. Its growth is suppressed considerably by Reaction 34 in the C_2H_2–HCl system, the yields of allene, propyne, and benzene decreasing.

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_5 \xrightarrow{C_2H_2} C_6H_7,$$

$$C_6H_7 \longrightarrow C_3H_3 \xrightarrow{C_2H_2} C_3H_4,$$

$$\longrightarrow C_6H_6.$$

The reactions with HCl would produce excess atoms than in its absence. The yields of hydrogen will increase by

$$H + C_2H_2 \longrightarrow H_2 + C_2H.$$

Apparently a different effect of hydrogen chloride on the two groups would result from the same radical scavenging by hydrogen chloride. The main and characteristic features of acetylene pyrolysis inhibited by hydrogen chloride can be explained by the free-radical mechanism.

Comparison with Other Inhibitors. The small inhibitory effect of nitrogen monoxide was interpreted in terms of the scavenging and partial revival of the chain carrier radical.[3]

$$C_4H_4(2) + NO \longrightarrow C_2HCHO + HCN, \qquad (36)$$

$$C_2HCHO \longrightarrow C_2H + CHO. \qquad (37)$$

By a comparison with the estimated rate constants for Reactions 11 and 36, we get

$$k_{36}/k_{11} = 2.4\times10^{-2}\exp(9300/RT). \qquad (38)$$

In the temperature range 1100—1350 K, the above values are 0.1—0.3, the scavenging effect of nitrogen monoxide being much smaller than that of hydrogen chloride. In the C_2H_2–NO system the steady-state concentration of $C_4H_3(2)$ radical is less reduced by Reaction 36, Reaction 8 being the predominant termination reaction.

The consumption rate of acetylene at temperatures below 800 K is inversely proportional to the hydrogen bromide concentration, while it is less dependent on the concentration of hydrogen chloride.[1] The activation energy of Reaction 11 is much greater than that of Reaction 8 (recombination reaction). Thus Reaction 8 can be faster than Reaction 11 at temperatures below 800 K, the scavenging effect of Reaction 11 being smaller. When hydrogen chloride is added in much smaller amounts than those in the present experiments. Reaction 8 predominates over Reaction 11 even at temperatures 1100—1350 K. In this case the inhibitory effect of hydrogen chloride would be similar to that reported.[1]

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5) The least-squares method gives log $A_1=12.46\pm0.33$, $E_1=45800\pm1900$, log $A_2=16.00\pm0.51$, and $E_2=67200\pm3000$, where A, E, and errors denote frequency factor, activation energy, and standard deviation of the least-squares method, respectively.

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7) The heats of formation, ΔH°(kcal/mol), are calculated at 298 K, the same heats of formation as those adopted[3]

being used. a) The heats of formation for HCl, Cl, and C_2HCl are -22.1, 28.9, and 51.1 kcal/mol. "JANAF Thermochemical Tables," 2nd ed, National Bureau of Standards NSRDS-NBS 37, U. S. Government Printing Office, Washington D. C. (1971); b) The heat of formation for C_2H_3Cl is 5.0 kcal/mol. Z. B. Alfassi, D. M. Golden, and S. W. Benson, *J. Chem. Thermodyn.*, **5**, 411 (1973); c) The heat of formation for $C_4H_3(2)Cl$ is estimated assuming the bond dissociation energy of C_4H_3–Cl is the same as that of C_2H_3–Cl (83.5 kcal/mol).

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11) In analogy with the reaction of CH_3+HCl, the activation energy of Reaction 11′ would be estimated as 5.4 kcal/mol from the heat of reaction. If the contribution of Reaction 11′ to the rate of Reaction 11 is far greater than that of Reaction 11′, the activation energy of Reaction 11 would be close to that of Reaction 11′. In the product analysis no detectable amount of chlorine atom containing products except for C_2HCl was found. This might indicate the minor role of reactions with Cl atom in spite of their smaller heats of reaction.

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