CHEMISTRY LETTERS, pp. 437-440, 1972. Published by the Chemical Society of Japan

PHOTOCHEMICAL AND RADIATION-INDUCED REACTIONS OF ACETYLENE AND HYDROGEN SULFIDE MIXTURE. SYNTHESIS OF THIOPHENE

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The ultraviolet irradiation of hydrogen sulfide in the presence of acetylene gives rise to a cyclic compound, thiophene, in addition to straight chain compounds already reported. In the photolysis or radiolysis of acetylene containing a small amount of hydrogen sulfide, the yield of benzene decreases while thiophene increases with increasing amounts of hydrogen sulfide.

Decomposition of Hydrogen Sulfide in the Presence of Acetylene. Photochemical and radiation-induced additions of hydrogen sulfide or thiols to olefins have been studied extensively,[1] but addition to acetylene has received far less attention.[2,3] Strausz[2] found that the major product of the reaction of C_2H_2-H_2S mixture exposed to the radiation with a medium pressure mercury arc in the liquid phase at -78°C was CH_2=CHSH and minor were H_2, polymer, CS_2, saturated mercaptan, olefins, and dithiols.

In our experiment, the direct-photolysis of C_2H_2-H_2S mixture at 2537Å (Table 1), thiophene was formed in a good yield in addition to the above products. In this condition, only hydrogen sulfide absorbs the light and decomposes as follows,

$$H_2S + h\nu \longrightarrow H + HS$$

While, it has been known that the reaction of H atom,[4-7] Cl atom,[8] or CH_3 radical[9] with acetylene forms benzene as one of the products. The reaction mechanism fits with the scheme,

$$X + C_2H_2 \longrightarrow C_2H_2X$$

$$C_2H_2X + C_2H_2 \longrightarrow C_4H_4X$$

$$C_4H_4X + C_2H_2 \longrightarrow CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}X$$

$$CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}X \longrightarrow \overbrace{CH{=}CH{-}CH{=}CH{-}CH{=}CH} + X$$

where X = H, Cl, CH_3.

Thus, a probable mechanism of thiophene formation is the following radical process.

$$SH \xrightarrow[+2C_2H_2]{} CH{=}CH{-}CH{=}CH{-}SH$$

$$CH{=}CH{-}CH{=}CH{-}SH \longrightarrow \overbrace{CH{=}CH{-}CH{=}CH{-}S} + H$$

Table 1. THE AMOUNT OF THIOPHENE FORMED IN THE DIRECT PHOTOLYSIS OF C_2H_2-H_2S MIXTURE AT 2537Å

C_2H_2 (mmHg)	H_2S (mmHg)	C_4H_4S ($\times 10^4$ μmol/min)
50.5	59.4	66.5
109	60.1	195
223	57.5	476
300	60.0	687

If it is true, it would be predicted that furan may be formed in the reaction of OH radical with acetylene and pyrrole in the reaction of NH_2 radical.

$$OH \xrightarrow[+2C_2H_2]{} CH{=}CH{-}CH{=}CH{-}OH$$

$$CH{=}CH{-}CH{=}CH{-}OH \longrightarrow \overbrace{CH{=}CH{-}CH{=}CH{-}O} + H$$

$$NH_2 \xrightarrow[+2C_2H_2]{} CH{=}CH{-}CH{=}CH{-}NH_2$$

$$CH{=}CH{-}CH{=}CH{-}NH_2 \longrightarrow \overbrace{CH{=}CH{-}CH{=}CH{-}NH} + H$$

In fact, pyrrole was formed in a small amount in the radiolysis and photolysis of C_2H_2-NH_3 mixture, but furan was not found in the reaction of C_2H_2-H_2O mixture. However, the formation of pyrrole can not necessarily support the reaction mechanism. Detailed discussion is withheld, until more extensive studies are carried out.

Decomposition of Acetylene in the Presence of Hydrogen Sulfide. When hydrogen sulfide was added as a scavenger in the radiolysis or mercury-sensitized photolysis of acetylene, the yield of benzene, a major product, decreased and thiophene was formed (Table 2, 3). At the hydrogen sulfide concentrations used in these experiments, energy

of the active ray is absorbed almost completely by acetylene.

The mechanism of thiophene formation in this case is uncertain, because the reaction mechanisms in the photolysis and radiolysis of pure acetylene have not yet been determined.[7,10]

Table 2. THE AMOUNTS OF BENZENE AND THIOPHENE FORMED IN THE MERCURY-PHOTOSENSITIZATION OF C_2H_2 CONTAINING H_2S[a)]

H_2S (mmHg)	C_6H_6 ($\times10^3\mu$mol/min)	C_4H_4S ($\times10^3\mu$mol/min)
0.00	386	0.00
0.47	123.2	187.8
1.04	57.8	125.0
10.46	5.76	55.6

a) C_2H_2 initial pressure 100 mmHg

Table 3. THE G-VALUES OF BENZENE AND THIOPHENE IN THE γ-RADIOLYSIS OF C_2H_2 CONTAINING H_2S[a)]

H_2S (mmHg)	$G(C_6H_6)$	$G(C_4H_4S)$
0.00	12.0	0.00
0.22	1.34	9.47
0.97	0.40	8.58
3.45	0.28	8.11
6.61	0.25	7.20

a) C_2H_2 initial pressure 100 mmHg

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(Received April 3, 1972)