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The Reactions of Acetylene Photosensitized by Cd($^3P_1$)

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The reactions of acetylene photosensitized by Cd($^3P_1$) have been investigated at 270±1°C. The main products were benzene and vinylacetylene. The formations of polymer and hydrogen were not observed. From the studies of the effects of pressures and foreign gases on the quantum yields, the product formations were successfully explained by the reactions of excited molecules. The investigation of the reaction of a mixture of hydrogen and acetylene photosensitized by Cd($^3P_1$) suggests that benzene is also formed from the reactions of hydrogen atoms and acetylene molecules.

Since Bates and Taylor investigated the reactions of acetylene photosensitized by mercury,[1] many investigations have been made of the reactions of this compound.[2-8] However, the mechanism of benzene formation has not yet been completely resolved. LeRoy has proposed a radical mechanism for the benzene formation,[7] while Shida and Tsukada have proposed a mechanism involving both free radicals and excited molecules.[8]

If benzene is formed only from the reaction of free radicals, its formation is not expected in the cadmium-photosensitization, because the dissociation energy of the C–H bond of the acetylene molecule (114 kcal)[9] is larger than the energy of triplet cadmium (87.7 kcal) even when the heat of the formation of cadmium hydride (15.5 kcal) is considered.

In the present paper, a detailed investigation of the reactions of acetylene photosensitized by cadmium will be reported.

Experimental

Acetylene, ethylene, isobutene, and *cis*-2-butene supplied by the Takachiho Shoji Co. were used after bulb-to-bulb distillations. The gas-chromatographic analysis showed that the impurities were less than 0.5%. Hydrogen supplied by the Suzuki Shokan Co. was used after it had been passed through a trap at the temperature of liquid nitrogen. Acetylene-d_2 was synthesized from calcium carbide and deuterium oxide. Mass-spectrometric analysis showed that the isotopic purity was larger than 98%.

The apparatus and the light source used were practically the same as have been described previously.[10]

The reaction products were analyzed by gas chromatography. The column used was packed with silicon DC-550 on celite (supplied by the Shimazu Co., 7 m long) and was operated at 60°C.

The intensity of the cadmium resonance line at 3261 Å was measured using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene under the assumption of the quantum yield being 0.5.[10]

Results and Discussion

Mechanism of Product Formations. In the reaction of acetylene photosensitized by cadmium at 270±1°C, the main products were identified as benzene and vinylacetylene by gas chromatography and by mass spectrometry. No hydrogen formation was observed; if present at all, the quantum yield is less than 10^{-5}.

Figure 1 shows the irradiation-time dependence of the products. A slight disappearance of acetylene was observed; the amount was almost equal to the sum of three times the amount of benzene and twice the amount of vinylacetylene. This fact suggests that the formation of polymers, such as cuprene, is negligibly small.

The isotopic hydrogen-atom distribution of benzene formed in the reaction of a mixture of acetylene-d_0 and -d_2 could not be determined, because intermolecular hydrogen-deuterium exchange reaction occurred rapidly, even in a dark reaction at 270±1°C.

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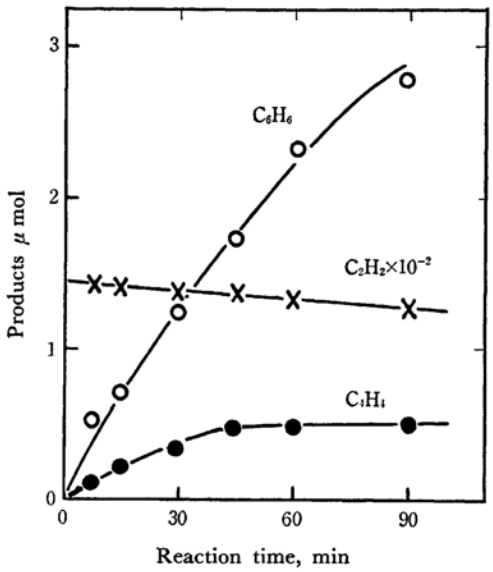

Fig. 1. Time dependence of the amounts of the products. (initial pressure, 36.6 mmHg)

Table 1 shows the quantum yields of the products formed in the reaction of acetylene at 80 mmHg, together with those in the presence of foreign gases.

The products of the cadmium-photosensitization are different from those of the mercury-photosensitization,[1-8] the direct photolysis,[11] and the radiolysis.[12] If benzene and vinylacetylene are formed from the reaction of free radicals, the formations of ethylene, 1,3-butadiene, and diacetylene can be expected, besides the formation of vinylacetylene. However, they were not observed in the cadmium-photosensitization. Furthermore, the energy available for the C–H-bond splitting in the cadmium-photosensitization is smaller than the dissociation energy of the C–H bond of the acetylene molecule. Benzene and vinylacetylene may be formed from the reaction of excited molecules. The energy levels of the excited singlet molecule are above the excitation energy of triplet cadmium.[13] The triplet state of the acetylene molecule is not known, although Bowman and Miller observed a peak at 2.0 eV in the electron-energy-loss spectrum of acetylene and tentatively surmised that the peak was caused by the triplet state of the acetylene molecule.[14]

Pressure-dependence of the Products. The quantum yields of benzene and vinylacetylene formations were measured over the pressure range from 10 to 330 mmHg (Fig. 2). Their maximum values were found at about 80 mmHg and at about 40 mmHg respectively. Even at the maximum values, the sum of their quantum yields is less than unity. That is, most of the energy absorbed by cadmium atoms is not used for the product formations. This fact can not be explained by the incomplete quenching of triplet cadmium atoms by acetylene, because the quenching efficiency of acetylene is almost equal to that of 2-butene[15] and the pressure range used here is the complete quenching region for 2-butene.[10]

To explain the pressure dependence of the quantum yields, the following reaction mechanism may be considered in terms of the excited molecules:

$$Cd(^3P_1) + A \rightarrow CdA^* \quad (1)$$
$$CdA^* \rightarrow Cd + A_1^* \quad (2)$$
$$CdA^* + A \rightarrow Cd + 2A \quad (3)$$
$$A_1^* + A \rightarrow A_2^* \quad (4)$$
$$\rightarrow 2A \quad (5)$$
$$A_2^* \rightarrow 2A \quad (6)$$
$$A_2^* + A \rightarrow A_3^* \quad (7)$$
$$A_3^* \rightarrow 3A \quad (8)$$
$$\rightarrow C_4H_4 + A \quad (9)$$
$$\rightarrow C_6H_6 \quad (10)$$
$$A_3^* + A \rightarrow C_6H_6 + A \quad (11)$$

TABLE 1. EFFECTS OF FOREIGN GASES ON THE PRODUCT FORMATIONS*

Foreign gas	mmHg	Products (quantum yield × 10²)					
		H_2	C_2H_6	C_2H_4	C_4H_4**	C_4H_6***	C_6H_6
	0	nil	nil	nil	2.0	nil	9.4
C_2H_4	10.1	nil	nil	—	0.4	nil	2.0
iso-C_4H_8	2.2	nil	nil	nil	—	—	2.2
H_2	110.	—	0.7	44.0	1.8	2.3	32.

* pressure of acetylene: 80 mmHg
** C_4H_4: vinylacetylene
*** C_4H_6: 1,3-butadiene

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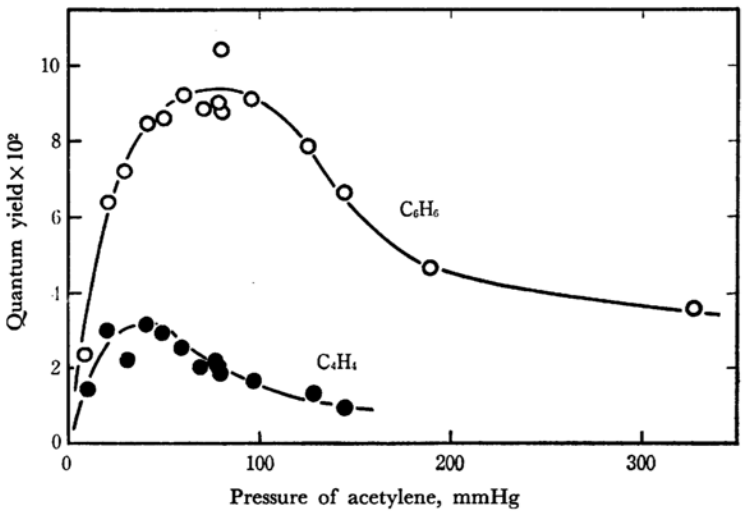

Fig. 2. Pressure dependence of the quantum yields of benzene and vinylacetylene formation.

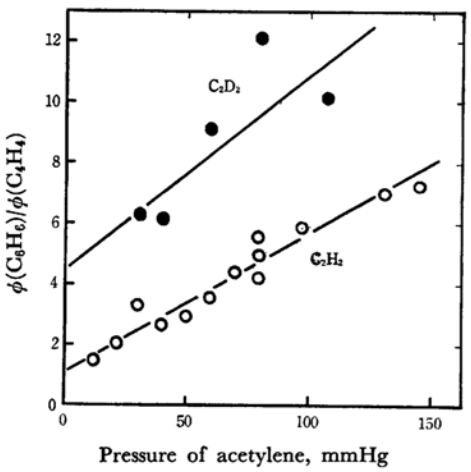

Fig. 3. Plots of the ratio, $\phi(C_6H_6)/\phi(C_4H_4)$ against the pressure of acetylene.

where acetylene is denoted as A and where CdA* is the transient complex of a triplet cadmium atom and an acetylene molecule. The symbols A_1*, A_2*, and A_3* represent, respectively, an excited acetylene molecule (presumably, a triplet acetylene molecule), a transient dimer, and a transient trimer. The steady-state treatment derives the following relation:

$$\phi(C_6H_6)/\phi(C_4H_4) = k_{10}/k_9 + (k_{11}/k_9)[A] \qquad (I)$$

where $\phi(C_6H_6)$ and $\phi(C_4H_4)$ are the quantum yields of the benzene and vinylacetylene formations respectively. The plots of the $\phi(C_6H_6)/\phi(C_4H_4)$ ratio *vs.* the acetylene pressure are shown in Fig. 3. From the slopes and the intercepts, the k_{10}/k_9 and k_{11}/k_9 values are calculated by the method of least squares (Table 2).

TABLE 2. VALUES OF k_{10}/k_9 AND k_{11}/k_9

	k_{10}/k_9	k_{11}/k_9 (mmHg^{-1})
C_2H_2	1.2±0.3	4.6±0.4
C_2D_2	4.6±2.1	6.5±3.0

Effects of Ethylene and Isobutene. As is shown in Table 1, ethylene and isobutene inhibit the formations of benzene and vinylacetylene. Figure 4 shows the plots of ϕ_0/ϕ *vs.* the foreign gas pressure in the reaction of acetylene at 80 mmHg. Here, ϕ_0 and ϕ are the quantum yields of benzene or vinylacetylene formations in the absence and in the presence of foreign gas respectively. The efficiency of isobutene for the inhibition is about five times that of ethylene. A similar trend has been reported in the efficiency of quenching

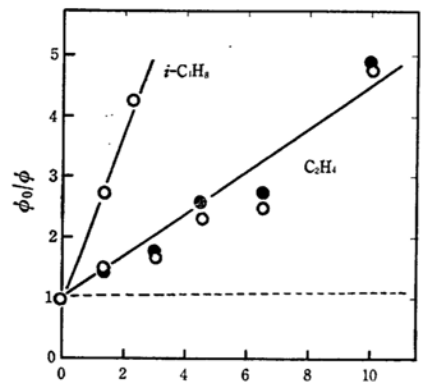

Fig. 4. Plots of ϕ_0/ϕ against the pressure of foreign gas.
(dotted line: expected curve from competitive quenching for Cd($^3P_1$) atoms, pressure of acetylene: 80 mmHg, ○: benzene, ●: vinylacetylene)

triplet benzene (about five times)[16,17] and triplet acetone (about four times),[18] and also in the efficiency of scavenging hydrogen atoms (about five times).[19]

The inhibition by ethylene or isobutene can not be explained by the competitive quenching for triplet cadmium atoms, since the observed $(\phi_0/\phi-1)$ values, as is shown in Fig. 4, are more than forty times as large as that calculated by assuming competitive quenching. The products expected by the addition of ethylene and isobutene were not detected in spite of careful research. The inhibition, therefore, may be explained by the quenching of excited molecules by foreign gases. Including the quenching reactions by foreign gases, the following relations are obtained:

$$(\phi_0/\phi)_{C_4H_4} = (1+k_{10}'[M]/(k_{10}+k_{11}[A]))(\phi_0/\phi)_{C_6H_6}$$
$$= (1+k_{11}'[M]/(k_8+k_9+k_{10}+k_{11}[A]))(1+k_7'[M]/(k_6+k_7[A]))(1+k_5'[M]/(k_4+k_5)[A])$$
$$\times (1+k_3'[M]/(k_2+k_3[A])) \quad \text{(II)}$$

Here, k_3', k_5', k_7', and k_{11}' represent, respectively, the rate constants of a foreign gas (M) for quenching CdA*, A_1*, A_2*, and A_3*.

As is shown in Fig. 4, the (ϕ_0/ϕ) value for vinylacetylene formation is almost equal to that for benzene formation; therefore, the $k_{11}'[M]/(k_{10}+k_{11}[A]) \ll 1$ relation holds under the conditions of this experiment. That is, the process of quenching A_3* by foreign gas is not effective for the inhibition of the formation of benzene and vinylacetylene. However, the linear relationship in Fig. 4 suggests that one of the quenching processes (reaction (3'), (5'), or (7')) is effective. However, no definite conclusion can be drawn as to which quenching process is the most effective on the basis of these experiments alone.

Isotope Effect. As is shown in Table 3, there are large isotope effects on the formations of benzene and vinylacetylene. In the mercury-photosensitization, no such large isotope effect has been observed on the formation of benzene.[8] The isotope effect can not be explained by the difference in the quenching efficiencies of acetylene-d_0 and -d_2.[15] The effect may result from the isotope effect on the rates of the reactions (9), (10), and (11), as is shown in Table 2.

Table 3. Isotope effects on the formations of benzene and vinylacetylene

Pressure mmHg	C_4H_4/C_4D_4	C_6H_6/C_6D_6
30	2.6	1.4
40	3.5	1.5
60	3.8	1.5
80	4.3	1.9
100	3.5	1.9

Effect of Hydrogen. As is shown in Table 1, the addition of an excess amount of hydrogen caused an increase in the quantum yield of benzene formation, together with those of ethylene and 1,3-butadiene formations. Cashion and LeRoy observed a similar effect of the addition of hydrogen in the mercury-photosensitization and proposed the importance of free radicals in the mechanism.[4] Benzene formed from the reaction of a mixture of acetylene-d_2 and hydrogen photosensitized by cadmium consisted of a mixture of C_6D_6(69.2%), C_6HD_5(26.6%), and $C_6H_2D_4$(3.5%). This suggests that a part of the benzene is formed by the reaction of hydrogen atoms. The reaction mechanism may be described as follows;

$$Cd(^3P_1) + H_2 \rightarrow CdH + H \quad (12)$$
$$H + C_2H_2 \rightarrow C_2H_3 \quad (13)$$
$$2\,C_2H_3 \rightarrow C_2H_2 + C_2H_4 \quad (14)$$
$$\rightarrow C_4H_6 \quad (15)$$
$$C_2H_2 + C_2H_2 \rightarrow C_4H_5 \quad (16)$$
$$2\,C_4H_5 \rightarrow C_4H_4 + C_4H_6 \quad (17)$$
$$\rightarrow \text{dimer} \quad (18)$$
$$C_4H_5 + C_2H_2 \rightarrow C_6H_7 \quad (19)$$
$$C_6H_7 \rightarrow C_6H_6 + H \quad (20)$$
$$\rightarrow \text{polymer} \quad (21)$$

This reaction mechanism interprets the formations of butadiene and ethylene as well as the formation of benzene. That is, benzene can also be formed from the reaction of free radicals.

The authors are indebted to Mr. H. Sakurai for the mass spectrometric analyses and to Mr. S. Hirokami for synthesizing acetylene-d_2.

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