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Mercury-Photosensitized Reaction of Acetylene

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The mercury-photosensitized reaction of acetylene has been studied with equimolar mixtures of C_2H_2 and C_2D_2 under various conditions of pressure, temperature, and additives. It is shown that the distribution of isotopically substituted benzenes can be explained by a modified excited state mechanism equally as well as, or more favourably than by the free radical mechanism. The results on deuterium-acetylene mixtures photosensitized by $Hg(^3P_1)$, however, suggest that benzene is also formed by the reaction of hydrogen atoms and acetylene molecules. The rates of benzene formation and of the polymer formation increased gradually with pressure in low pressure region to attain a maximum and then decreased. Argon very strongly inhibited the benzene formation and, to a less extent, the polymer formation. The primary process is explained by assuming the formation of a transient complex of a triplet mercury atom and an acetylene molecule.

Since the early work of Bates and Taylor,[1] photopolymerization of acetylene has been the subject of a number of studies. In spite of the simplicity of the over-all reaction, which produces mainly benzene and an involatile solid polymer, cuprene, no final agreement on the mechanism of the reaction has yet been attained, although the free radical mechanism appears to be predominant at the present stage. For the formation of benzene, an excited molecule mechanism was suggested for the mercury-photosensitized reaction,[2] though LeRoy and Steacie[3] proposed a free radical mechanism to explain the formation of polymer and volatile products from the fact that nitric oxide inhibited the polymerization. Mains, Niki and Wijnen[4] found that isotopic benzenes including an odd number of H or D atoms were produced in significant yields in mercury-photosensitization of C_2H_2-C_2D_2 mixtures, suggesting a free radical mechanism again. However, the observed distribution of isotopic benzenes can not necessarily support the free radical mechanism, which can also be explained by a modified excited molecule mechanism.[5]

Experimental

Acetylene (purity, 99.6%) supplied by Takachiho Trading Co. was passed through a silica gel column and further through a trap immersed in a carbon dioxide-acetone mixture followed by bulb-to-bulb distillation, and the middle third was used. No impurity was detected by gas chromatography or by mass spectrometry. Acetylene-d_2 was prepared by passing D_2O through high-purity carbide, purified with a dimethyl sulfolane column and degassed by bulb-to-bulb distillation. Less than 1.3% C_2HD was found as an impurity. Nitric oxide and argon (Takachiho Trading Co., purity, 98.5 and 99.999% respectively) were used without further purification.

The light source was a low-pressure mercury resonance lamp. Between the lamp and the quartz reaction vessel, a UV-25 filter (Toshiba Denki Co.) which eliminated a light shorter than 2300 Å was placed. The reactant was circulated through a closed loop system having a mercury vapor saturator and a glass pump circulator. Total pressure change was measured with a mercury manometer and a travelling microscope.

Benzene formed as a product was analyzed by gas chromatography under reduced pressure. The column used was packed with dioctyl phthalate at 80°C. The distribution of isotopically substituted benzenes was analyzed by means of a mass spectrometer using ionizing electrons of 10 eV which produce almost only the parent ions of benzenes.

Results and Discussion

Reaction Products. The products formed from C_2H_2 were hydrogen, diacetylene, vinylacetylene, benzene, cyclooctatetraene, polymer, and C_2HD in the case of C_2H_2-C_2D_2 mixtures. No attempt was made to measure quantitatively other products except for benzene, C_2HD, and polymer, since it was confirmed that they were formed only in very small amounts. These products are in general accord with those found by

1) J. R. Bates and H. S. Taylor, *J. Amer. Chem. Soc.*, **49**, 2438 (1927).
2) S. Shida, Z. Kuri and T. Furuoya, *J. Chem. Phys.*, **28**, 131 (1958).
3) D. J. LeRoy and E. W. R. Steacie, *ibid.*, **12**, 117 (1944).
4) G. J. Mains, H. Niki and M. H. J. Wijnen, *J. Phys. Chem.*, **67**, 11 (1963).
5) S. Shida, M. Tsukada and T. Oka, *J. Chem. Phys.*, **45**, 3483 (1966).

Table 1. Distribution of isotopic benzenes formed in the mercury-photosensitized reaction of C_2H_2-C_2D_2 mixtures

Acetylene initial press. mmHg	9.4	14.2	24.0	36.0	49.0	118.0
C_6H_6	8.3%	8.4%	9.2%	9.0%	9.8%	10.0%
C_6H_5D	8.4	7.1	6.8	7.0	6.5	6.4
$C_6H_4D_2$	26.2	26.4	25.9	27.0	27.4	28.9
$C_6H_3D_3$	17.7	14.3	13.9	13.7	12.5	12.0
$C_6H_2D_4$	23.8	27.1	26.4	27.1	28.1	28.2
C_6HD_5	9.7	7.3	7.4	7.1	6.1	5.7
C_6D_6	7.6	9.5	10.2	9.1	9.6	8.8

earlier workers.[2,3,6]

Isotopic Studies. The mercury-photosensitized reaction of an approximately equimolar mixture of C_2H_2 and C_2D_2 resulted in the mixture of isotopically substituted benzenes shown in Table 1. The yields of C_6H_5D, $C_6H_3D_3$, and C_6HD_5 are too large to be accounted for by statistical inclusion of C_2HD, because the concentration of C_2HD formed is nearly less by a few per cent of the initial acetylene.[7] It can be seen that the yields of C_6H_6, $C_6H_4D_2$, $C_6H_2D_4$, and C_6D_6 are relatively larger than those of C_6H_5D, $C_6H_3D_3$, and C_6HD_5, and that the distribution of isotopic benzenes is almost constant at higher pressures.

As suggested by LeRoy,[8] this isotopic distribution may be explained by a free radical mechanism initiated by hydrogen atoms such as

$$\left.\begin{aligned} &C_2H_2 + H \rightarrow C_2H_3 \\ &C_2H_3 + C_2H_2 \rightarrow C_4H_5 \\ &C_4H_5 + C_2H_2 \rightarrow C_6H_7 \\ &C_6H_7 \rightarrow C_6H_6 + H \end{aligned}\right\} \quad (I)$$

The distribution of various benzenes predicted on the basis of the free radical mechanism (I) would be, in decreasing order of H atom content, 9.4%, 6.25%, 28.2%, 12.5%, 28.2%, 6.25%, 9.4%. The calculation is performed on the assumption that the quenching cross sections for the formation of H or D atoms from C_2H_2 and C_2D_2 are equal and that the probability of eliminating a D or H atom from a terminal =CHD group on cyclization is 0.5. The calculated percentages are nearly in agreement with the distributions except for those in the low pressure region.

As shown in Table 1, the observed distribution depends on the acetylene pressure in the low pressure region and the yields of benzenes containing an odd number of D atoms tend to increase as the acetylene pressure decreases.[9] The distribution of isotopic benzenes expected to be formed in the radical mechanism should be independent of the acetylene pressure. Thus, the free radical mechanism could not explain the change of the isotopic distribution at low pressures. The close agreement between the distribution observed in the higher pressure region and the calculated one can not necessarily support such a radical mechanism.

The observed distribution can be as well accounted for by a modified excited molecule mechanism as by the radical mechanism.[5] This mechanism which involves redissociation of a hot acetylene dimer molecule is shown as follows:

$$\left.\begin{aligned} &C_2H_2^* + C_2H_2 \rightarrow \begin{matrix} CH{=}CH^* \\ | \quad | \\ CH{=}CH \end{matrix} \\ &\begin{matrix} CH{=}CH^* \\ | \quad | \\ CH{=}CH \end{matrix} \rightleftarrows \begin{matrix} CH{-}CH^* \\ \| \quad \| \\ CH{-}CH \end{matrix} \\ &\begin{matrix} CH{-}CH^* \\ \| \quad \| \\ CH{-}CH \end{matrix} \rightarrow C_2H_2^{**} + C_2H_2 \\ &C_2H_2^{**} \xrightarrow[+C_2H_2]{} C_4H_4^{**} \xrightarrow[+C_2H_2]{} C_6H_6 \end{aligned}\right\} \quad (II)$$

where * denotes highly (electronically or vibronically) excited states and ** lower excited states. In this mechanism, $C_2H_2^*$ and $C_2D_2^*$ will be in the ratio 1 : 1 and no C_2HD^* exists, but $C_2H_2^{**}$, C_2HD^{**}, and $C_2D_2^{**}$ are produced in the ratio 3 : 2 : 3 in an equimolar C_2H_2-C_2D_2 mixture. Consequently, the benzene formed *via* the path including excited acetylene would again consist of the distribution, 9.4%, 6.25%, 28.2%, 12.5%,

6) J. K. Cashion and D. J. LeRoy, *Can. J. Chem.*, **32**, 906 (1954).

7) Recently, Fujisaki *et al.* studied the radiolysis of C_2H_2-C_6D_6 mixtures and found that benzene formed was only C_6H_6. N. Fujisaki and S. Shida, unpublished. From this, it can be confirmed that the isotopic exchange between acetylene and benzene formed does not occur in the mercury-photosensitized reaction of C_2H_2-C_2D_2 mixtures.

8) D. J. LeRoy, *J. Chem. Phys.*, **45**, 3482 (1966).

9) In the direct-photolysis of acetylene at 1849 Å, the distribution of isotopic benzenes and the change of it at lower pressures was just the same as in mercury-photosensitization. S. Shida and M. Tsukada, unpublished. In the radiolysis, the distribution was the same as in mercury-photosensitization at higher pressures and was constant in the higher pressure region than 20 mm. S. Shida and T. Oka, unpublished.

28.2%, 6.25%, 9.4%. However, the distribution would be independent of acetylene initial pressure also in this case.

In the reaction mechanism (II), it may be assumed that C_4H_4** is unstable and decomposes into two acetylene molecules or further reacts with an acetylene molecule. If this is the case, C_4H_4** might dissociate into no two ground state acetylene molecules but give C_2H_2** molecule as follows:

$$C_4H_4^{**} \rightarrow C_2H_2^{**} + C_2H_2 \qquad \text{(III)}$$

If the mechanism including reaction (III) is assumed as

$$\left.\begin{aligned} &C_2H_2^{*} + C_2H_2 \rightarrow C_4H_4^{*} \\ &C_4H_4^{*} \rightarrow C_2H_2^{**} + C_2H_2 \\ &C_2H_2^{**} + C_2H_2 \rightarrow C_4H_4^{**} \\ &C_4H_4^{**} \rightarrow C_2H_2^{**} + C_2H_2 \\ &\qquad\qquad \rightarrow C_6H_6 \end{aligned}\right\} \qquad \text{(IV)}$$

the distribution of isotopic benzenes formed in C_2H_2-C_2D_2 mixture would be 8.6%, 7.8%, 25.8%, 15.6%, 25.8%, 7.8%, 8.6%.

If the reaction conforms to mechanism (II) at higher pressures and if the cyclobutadiene** molecules partially dissociate to give acetylene** molecules before coming into collision with acetylene at lower pressures, this mechanism would explain the result that the yields of isotopic benzenes containing an odd number of H or D atoms tend to increase at lower pressures. It seems that the modified excited state mechanism would be more favourable that the radical mechanism in this respect.

A fact which has been considered as a direct support for the radical mechanism is the benzene formation in the reaction of acetylene with hydrogen atom.[4,6] However, the formation of benzene in the Cd($^3P_1$)-photosensitized reaction of acetylene studied by Tsunashima and Sato[10] seems to strongly suggest that benzene is also formed by some excited molecule mechanism, because the dissociation energy of the C–H bond of acetylene molecule (114 kcal)[11] is larger than the energy of triplet cadmium (87.7 kcal) even when the heat of formation of cadmium hydride (15.5 kcal) is taken into account.

A single determination of isotopic cyclooctatetraene (COT) formed in the mercury-photosensitized reaction of C_2H_2-C_2D_2 mixture was also made (Table 2). If COT is formed from the reaction of free radicals as

$$H \xrightarrow[+4C_2H_2]{} C_8H_9$$

$$C_8H_9 \rightarrow C_8H_8 + H,$$

Table 2. Distribution of isotopic cyclooctatetraenes formed in the mercury-photosensitized reaction of C_2H_2-C_2D_2 mixtures[a]

C_8H_8	6.3%
C_8H_7D	2.1
$C_8H_6D_2$	23.1
$C_8H_5D_3$	4.6
$C_8H_4D_4$	32.6
$C_8H_3D_5$	3.5
$C_8H_2D_6$	21.3
C_8HD_7	1.1
C_8D_8	5.4

a) Acetylene initial pressure 574 mm

the isotopic distribution predicted will be 4.7%, 3.1%, 18.8%, 9.4%, 28.1%, 9.4%, 18.8%, 3.1%, 4.7%. But if COT is assumed to be formed from the reaction of C_6H_6*, the precursor of benzene, with C_2H_2, just the same distribution as above is predicted. Consequently, it is impossible to determine from the isotopic distribution of COT whether the free radical or the excited state mechanism is more favourable.

Effect of Acetylene Pressure. Figures 1 and 2, respectively, show the pressure depend-

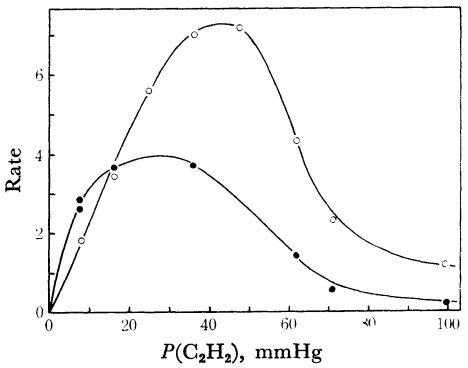

Fig. 1. Rates of formation of benzene and C_2HD.
—○— C_6H_6 ($\times 10^{-8}$ mol/min)
—●— C_2HD ($\times 10^{-7}$ mol/min)

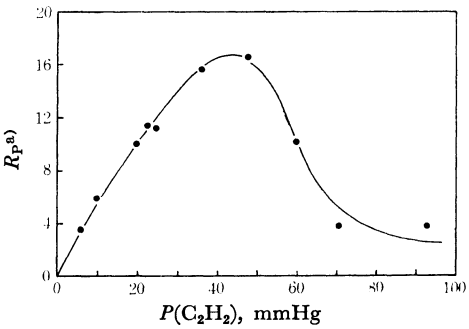

Fig. 2. Rate of polymer formation (acetylene consumed for cuprene).
a) $\times 10^{-7}$ mol/min

10) S. Tsunashima and S. Sato, This Bulletin, **41**, 2281 (1968).
11) B. E. Knox and H. B. Palmer, *Chem. Rev.*, **61**, 247 (1961).

ence of the rate of benzene formation and of the rate of polymer formation. The shapes of both the curves are very similar. The rates increase gradually with pressure in the low pressure region to attain a maximum and then decrease. This fact has not been noted by previous investigators.[2,3] Although mercury vapor may be consumed by some reaction with actylene,[3,12] the decrease of the rates in the higher pressure region can not be ascribed to the deficiency of mercury vapor, because a mercury saturator is used in the present experiment. A similar pressure dependence has also been found in the cadmium-photosensitized reaction[10] and also in the radiolysis[13,14] of acetylene.

Effect of Argon. Figure 3 shows the effect of the addition of argon on the rates. Argon very strongly inhibits benzene formation and, to a less extent, polymer formation. It is considered that mechanisms of both benzene and polymer formation include a certain excited intermediate in some stage of reaction, because argon acts only as the deactivator under the experimental conditions. It should be noted here that argon does not quench the excited mercury atom, because the quenching cross section of argon for $Hg(^3P_1)$ is almost zero while that of acetylene is much larger.

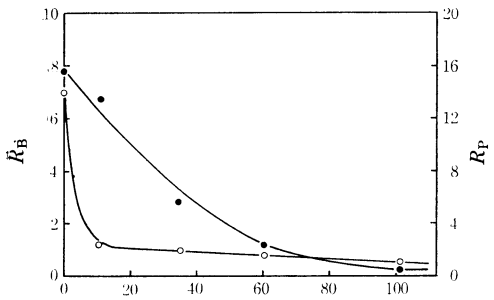

Fig. 3. Effect of argon on the rates of polymer formation and benzene formation.
—○— C_6H_6 ($\times 10^{-8}$ mol/min)
—●— Polymer Formation ($\times 10^{-7}$ mol/min)
Acetylene initial pressure 36.0 mmHg

Primary Process. If an initially excited acetylene decomposes to give an H atom and a C_2H as

$$\left.\begin{aligned} C_2H_2 + Hg^* &\rightarrow C_2H_2^* + Hg \\ C_2H_2^* &\rightarrow C_2H + H \end{aligned}\right\} \quad (V)$$

the formation of diacetylene C_4H_2 is to be expected. However, no significant amount of diacetylene was formed. It might be considered that C_2H radicals add to acetylene rather than recombine to give C_4H_2. But in the direct-photolysis of acetylene at 1849Å, diacetylene was formed as one of the major products as shown in Table 3. In the direct-photolysis, the initial absorption of light by acetylene leads to dissociation along with the formation of excited molecule, and C_4H_2 may be formed by the recombination of C_2H radicals.[15] Thus, the simple mechanism (V) is inadequate for the explanation of the initial stage of mercury-photosensitized reaction.

Table 3. Products in the direct-photolysis of acetylene at 1849 Å

C_2H_2 init. press. mmHg	C_6H_6[a]	C_4H_2[a]
11.0	1.8	6.3
36.0	3.5	4.5
64.5	3.7	4.1
92.0	4.8	3.8

a) $\times 10^{-8}$ mol/min

Sherwood and Gunning[16] showed that a stable mercury compound, probably a mercury carbide, is formed in the reaction and that enriched isotopic composition of ^{202}Hg was obtained in the solid reaction products under ^{202}Hg monoisotopic photosensitization. Furthermore, they studied the mercury-photosensitized decomposition of acetylene in the presence of nitric oxide using a fast-flow apparatus.[17] From the results they proposed the primary process

$$\left.\begin{aligned} Hg^* + C_2H_2 &\rightarrow HgH + C_2H \\ &\rightarrow HgC_2H + H \\ &\rightarrow Hg + C_2H_2^* \end{aligned}\right\} \quad (VI)$$

where $C_2H_2^*$ is not chemically reactive and only collisionally deactivated.

However, the deactivation effect of argon and the formation of only a small amount of diacetylene are probably not explained by a mechanism initially including the process (VI).

We suggest that the following primary sequence is in agreement with the observed data

$$\left.\begin{aligned} Hg^* + C_2H_2 &\rightarrow (HgC_2H_2)^* \\ (HgC_2H_2)^* &\rightarrow Hg + C_2H_2^* \\ &\rightarrow HgC_2H + H \\ (HgC_2H_2)^* + M &\rightarrow Hg + C_2H_2 + M \end{aligned}\right\} \quad (VII)$$

where $C_2H_2^*$ does not decompose to give an H atom any more.

12) H. W. Melville, *Trans. Faraday Soc.*, **32**, 258 (1935).
13) F. H. Field, *J. Phys. Chem.*, **68**, 1039 (1964).
14) J. H. Futrell and L. W. Sieck, *ibid.*, **69**, 892 (1965).
15) M. Zelikoff and L. M. Aschenbrand, *J. Chem. Phys.*, **24**, 1034 (1956).
16) A. G. Sherwood and H. E. Gunning, *Can. J. Chem.*, **38**, 466 (1960).
17) A. G. Sherwood and H. E. Gunning, *J. Phys. Chem.*, **69**, 1732 (1965).

TABLE 4. EFFECT OF NITRIC OXIDE, ARGON, AND TEMPERATURE ON THE DISTRIBUTION OF ISOTOPIC BENZENES[a)]

	Additives		Temp., °C		
	1.3% NO	61.2 mmHg	150	270	262[b)]
C_6H_6	7.9%	9.9%	7.7%	6.9%	5.6%
C_6H_5D	6.5	6.8	6.4	7.5	9.2
$C_6H_4D_2$	24.6	28.1	26.1	24.3	20.7
$C_6H_3D_3$	16.8	12.3	14.0	15.8	19.6
$C_6H_2D_4$	28.9	27.8	28.6	26.9	23.5
C_6HD_5	6.6	5.6	6.8	8.4	12.9
C_6D_6	8.8	9.5	10.4	10.2	8.7

a) Acetylene initial pressure 36.0 mmHg
b) Ref. 4

The primary process of photosensitization in which the photosensitizer interacts chemically or forms chemically reactive intermediates by bonding or complexing with the non-absorbing molecules can not always be distinguished from simple physical transfer of energy in collisions. However, it was suggested that a water molecule, for example, reacts with an excited mercury atom to give an excited complex, $(HgH_2O)^*$, which results in decomposition through a second collision with a third body.[18] In the cadmium($^3P_1$)-photosensitization, Tsushima and Sato[10] suggested the formation of the transient complex of a triplet cadmium atom and an acetylene molecule, $(CdC_2H_2)^*$.

As shown in Fig. 3, it seems that the deactivation effect of argon differs for polymer formation and benzene formation. From mechanism (VII), if excited species (some of $C_2H_2^*$, $C_2H_2^{**}$, $C_4H_4^*$, or $C_4H_4^{**}$) is deactivated in addition to the deactivation of $(HgC_2H_2)^*$, the rate of benzene formation will be much affected.

Using the method of the mercury-photosensitized decomposition of acetylene at very low pressure in the presence of excess amounts of helium, Kebarle[19] suggested that the primary decomposition of acetylene is very small which is about 7% of decomposition of ethylene having a similar quenching cross section. The deactivation of $(HgC_2H_2)^*$ based on analogous arguments as used above can interpret the fact.

Influence of Nitric Oxide. Effect of nitric oxide on the rates of pressure decrease and benzene formation is shown in Fig. 4. Nitric oxide largely suppresses the benzene formation. Nitric oxide usually behaves as a radical scavenger. But, at the same time, nitric oxide which is a paramagnetic molecule may quench the excited triplet species like oxygen.[20]

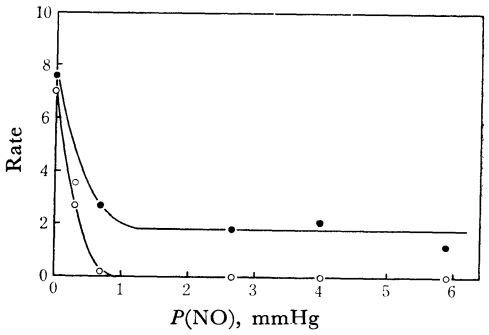

Fig. 4. Effect of nitric oxide on the rates of pressure decrease and of benzene formation.
—○— C_6H_6 ($\times 10^{-8}$ mol/min)
—●— Press. Decrease ($\times 10^{-2}$ mm/min)

Effect on Distribution of Isotopic Benzenes. Table 4 shows the effects of nitric oxide, argon, and temperature on the distribution of isotopic benzenes. Addition of nitric oxide or argon does not affect distribution so much, at least under the experimental conditions. It may be seen that the isotopic benzenes having an odd number of H or D atoms appreciably increase with the rise of temperature. On the basis of the modified excited state molecule mechanism shown above, the change of distribution can be understood on the assumption that the rate of decomposition of cyclobutadiene increases with the rise of temperature.

Effect of Hydrogen Atom. It is known that the hydrogen atom induces the polymerization of acetylene.[4,6,10] Table 5 shows the effect of addition of excess amount of D_2. Benzene formed from the reaction of C_2H_2-D_2 mixture photosensitized by Hg($^3P_1$) consists of a mixture of C_6H_6,

TABLE 5. ISOTOPIC BENZENES FORMED IN THE MERCURY-PHOTOSENSITIZED REACTION OF C_2H_2-D_2 MIXTURE

C_2H_2 (mmHg)	12	12
D_2 (mmHg)	300	494
C_6H_5D/C_6H_6	0.58	0.58

18) H. E. Gunning and O. P. Strausz, "Advances in Photochemistry," Vol. 1, ed. by W. A. Noyes, G. S. Hammond and J. N. Pitts, Interscience Publishers, New York (1963).
19) P. Kebarle, *J. Chem. Phys.*, **39**, 2218 (1963).
20) For example, G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, **27**, 18 (1959).

C_6H_5D and $C_6H_4D_2$. This suggests that a part of the benzene is actually formed by the reaction of hydrogen atoms.

Conclusion

The formation of benzene in the mercury-photosensitization of acetylene could be explained by a modified excited state mechanism equally as well as, or more favourably than, by the free radical mechanism on the basis of the distribution of isotopic benzenes. The effects of additives and of acetylene initial pressure suggest that the primary process is constituted including a transient complex of a triplet mercury atom and an acetylene molecule.