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Photolysis of Acetylene at 1849 Å

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The direct photolysis of acetylene produces mainly diacetylene, benzene, and solid polymers. For the formation of benzene, Zelikoff and Aschenbrand[1] suggested an excited-molecule mechanism. Meanwhile, for the mercury photosensitization both the the free radical mechanism[2,3] and the modified excited-molecule mechanism[4] were proposed and final agreement has not yet been attained. The present work was undertaken as a re-examination of the reaction mechanism of the direct photolysis.

Experimental

Preparation, purification and purity of acetylene, acetylene-d$_2$, and nitric oxide were similar to those described before.[5] The light source was a low-pressure mercury resonance lamp. The reactant was circulated through a closed loop system (volume=680 m*l*). Total pressure change was measured with a Bourdon gauge. Special precaution was taken to keep the vacuum line free of mercury. The products were analyzed by gas chromatography (dioctyl phthalate column at 80°C). The analytical method of isotopically substituted benzenes was the same as that used before.[5]

Results and Discussion

Figure 1 shows the pressure dependence of the rates of the major products. The distinct differences between the mercury-photosensitized reaction[5] and the direct photolysis are that diacetylene is one of the major products and that the pressure dependence curves of benzene and of polymer have no maximum in the direct photolysis.

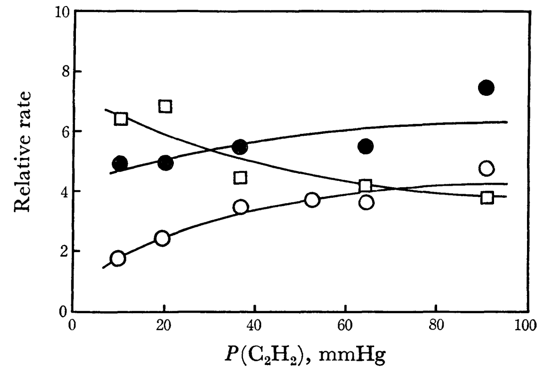

Fig. 1. Relative rate of product formation in the photolysis at 1849 Å against the acetylene pressure.

—○— C_6H_6 (10^{-8} mol/min)

—□— C_4H_2 (10^{-8} mol/min)

—●— Pressure decrease (10^{-2} mmHg/min)

Table 1 shows the distribution of isotopically substituted benzenes formed in equimolar C_2H_2–C_2D_2 mixtures. It can be seen that the yields of benzenes containing an odd number of H or D

TABLE 1. THE DISTRIBUTION OF ISOTOPIC BENZENES FORMED IN THE PHOTOLYSIS OF EQUIMOLAR C_2H_2-C_2D_2 MIXTURES AT 1849 Å

Acetylene initial pres. mmHg	6.0	9.5	13.8	19.5	27.7	39.7	71.3	100.7	Av.[a]	Calc.[b]
C_6H_6	6.7%	8.0%	7.6%	8.9%	9.7%	8.9%	9.1%	9.7%	9.4%	9.4%
C_6H_5D	8.6	7.3	7.5	6.8	7.0	6.6	6.6	5.7	6.5	6.25
$C_6H_4D_2$	22.0	23.6	24.5	24.8	24.8	27.0	26.9	27.5	26.6	28.2
$C_6H_3D_3$	17.7	16.3	15.1	14.0	13.2	12.5	12.2	10.9	12.2	12.5
$C_6H_2D_4$	26.0	26.5	27.7	27.6	27.5	28.5	28.4	29.1	28.4	28.2
C_6HD_5	9.2	9.2	8.0	7.3	7.0	6.7	7.0	6.3	6.8	6.25
C_6D_6	9.8	9.1	9.6	10.6	10.7	9.8	9.8	10.8	10.3	9.4

a) Average distribution (of column 6, 7, 8, and 9).

b) Calculated from molecular mechanism, (1), (2), (3), and (5).

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[1] M. Zelikoff and L. M. Aschenbrand, *J. Chem. Phys.*, **24**, 1034 (1956).

[2] D. J. LeRoy and E. W. R. Steacie, *ibid.*, **12**, 117 (1944).

[3] D. J. LeRoy, *ibid.*, **45**, 3482 (1966).

[4] S. Shida, M. Tsukada, and T. Oka, *ibid.*, **45**, 3483 (1966).

[5] S. Shida and M. Tsukada, This Bulletin, **43**, 2740 (1970).

atoms are relatively large from the view-point of simple molecular mechanism and that the distribution is almost constant at higher pressures.

The distribution observed here may be quantitatively explained by the free radical mechanism initiated by hydrogen atom as suggested for the mercury photosensitization by LeRoy,[3] but it can be accounted for as well by the modified excited-molecule mechanism[4,5]; the isotopic distribution predicted on the basis of either mechanism is quite the same (Table 1, the last column).

In low pressure region, however, the observed distribution depends on the acetylene pressure (Table 1) and the yields of benzenes containing an odd number of H or D atoms tend to increase with decreasing acetylene pressure in the same manner as in the mercury photosensitization.[5] The free radical mechanism could not explain the change of the distribution at low pressures, because the distribution expected from the mechanism should be independent of the acetylene pressure.

If an excited acetylene dimer molecule is assumed to repeat dissociation and regeneration to form an excited acetylene molecule at low pressures as follows,

$$C_2H_2^* + C_2H_2 \rightarrow C_4H_4^* \qquad (1)$$

$$C_4H_4^* \rightarrow C_2H_2^{**} + C_2H_2 \qquad (2)$$

$$C_2H_2^{**} + C_2H_2 \rightarrow C_4H_4^{**} \qquad (3)$$

$$C_4H_4^{**} \rightarrow C_2H_2^{**} + C_2H_2 \qquad (4)$$

$$C_4H_4^{**} + C_2H_2 \rightarrow C_6H_6 \qquad (5)$$

where $C_2H_2^{**}$ and $C_4H_4^{**}$ mean lower excited molecules, the yields of benzenes containing an odd number of H or D atoms should increase.

Figure 2 shows the effects of the addition of nitric oxide on the rate of pressure decrease and of product formation. Nitric oxide markedly suppresses the benzene formation. But this effect of nitric oxide on the benzene formation does not necessarily indicate the radical mechanism. It would be considered that the excited singlet acetylene is converted into the triplet state and the latter initiates the benzene formation. If it is the case, nitric oxide could quench the triplet acetylene.[6]

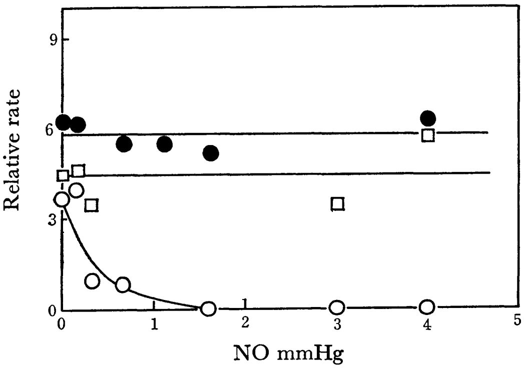

Fig. 2. Effect of nitric oxide on the relative rate of product formation. Acetylene initial pressure 37 mmHg.
—○— C_6H_6 (10^{-8} mol/min)
—□— C_4H_2 (10^{-8} mol/min)
—●— Pressure decrease (10^{-2} mmHg/min)

The diacetylene formation is not influenced practically by nitric oxide, but it has been found that ethynyl radicals do not react with NO.[7] Thus, it can be considered that diacetylene is produced by the radical reaction of ethynyl radicals.

Summarizing the above results, a possible reaction mechanism is depicted as follows.

$$C_2H_2 + h\nu \rightarrow C_2H_2^*$$

$$C_2H_2^* \rightarrow C_2H + H$$

$$C_2H_2^* \xrightarrow[+2C_2H_2]{} C_6H_6$$

$$C_2H + C_2H \rightarrow C_4H_2$$

$$H + nC_2H_2 \rightarrow \text{Polymer}$$

$$C_2H + nC_2H_2 \rightarrow \text{Polymer}$$

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[6] For example, G. Porter and M. R. Write, *Discuss. Faraday Soc.*, **27**, 18 (1959).

[7] A. G. Sherwood and H. E. Gunning, *J. Phys. Chem.*, **69**, 1732 (1965).