

## SHORT COMMUNICATIONS

## Mechanism of Benzene Formation in the Radiation-Induced and Photochemical Reactions of Acetylene

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It is known that acetylene polymerizes to give benzene and solid polymers in radiation-induced and photochemical reactions. For the formation of benzene, radical mechanism<sup>1-4)</sup> and excited molecule mechanism<sup>5-11)</sup> have been proposed, but no decisive conclusion has been reached.

Table 1 shows the distribution of isotopic benzenes formed in equimolar  $C_2H_2$ - $C_2D_2$  mixtures. In mercury photosensitization<sup>10)</sup> and direct photolysis,<sup>11)</sup> the distribution is almost constant above 20 mmHg of acetylene pressure. In Table 1, distributions for photolyses are given by average values within this pressure range.

The distribution in radiolysis<sup>12)</sup> may be regarded as constant within the acetylene pressures applied and is almost the same as that in the mercury-photo-sensitized reaction and the direct photolysis at 1849 Å.

It has been shown that the distribution could be explained by a modified excited molecule mechanism<sup>10,11)</sup> as well as, or more favourably, by the free radical mechanism, for the photolytic reactions.

The results suggests that benzene is formed in the same mechanism irrespective of the kind of active rays. Detailed studies are in progress.

TABLE 1. DISTRIBUTIONS OF ISOTOPIC BENZENES FORMED IN MERCURY PHOTOSENSITIZATION, DIRECT PHOTOLYSIS AT 1849 Å AND THE GAMMA-RAY-INDUCED REACTION OF ACETYLENE

Acetylene initial press. mmHg	Radiolysis						Photolysis		
	20	40	69	105	299	503	Av.	Av. <sup>a)</sup>	Av. <sup>b)</sup>
$C_6H_6$	9.5%	9.5%	9.2%	9.0%	9.4%	9.5%	9.4%	9.4%	9.5%
$C_6H_5D$	6.7	6.7	6.8	6.9	6.4	6.4	6.7	6.5	6.7
$C_6H_4D_2$	28.5	28.6	28.2	28.0	28.8	28.9	28.5	26.6	27.3
$C_6H_3D_3$	12.3	12.3	12.9	13.3	12.1	12.1	12.5	12.2	13.0
$C_6H_2D_4$	28.0	28.0	28.0	27.8	28.2	28.4	28.1	28.4	27.5
$C_6HD_5$	5.8	5.8	6.0	6.3	5.8	5.7	5.9	6.8	6.6
$C_6D_6$	9.1	9.0	8.9	8.7	9.3	9.2	9.0	10.3	9.4

a) Photolysis at 1849 Å, see Ref. 11.

b) Mercury photosensitization, see Ref. 10.

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11) M. Tsukada and S. Shida, to be published in this Bulletin.

12) Isotopic exchange between acetylene and benzene formed was not considered to occur since the radiolysis of  $C_2H_2$ - $C_6D_6$  mixtures gave only  $C_6H_6$ .