21. Kinetics of Iodine Catalyzed Aromatic Bromination

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The most detailed experimental data on the iodine catalyzed bromination has been presented by Bruner[1] (Z. physik. Chem., **41**, 514 (1902)). He obtained fairly good constants of a second order with respect to bromine, but could not express in his formula how iodine participated in the reaction. Price[2] (JACS **58** 1834 (1936); *ibid.* 2101), taking into account his experimental results on the bromination of phenanthrene as well as Bruner's data, indicated the rate of reaction accurately as follows:

$$d[C_6H_5Br]/dt = k[C_6H_6][Br_2]^{3/2}[I_2]^{5/2}$$

Three years ago, Robertson[3] (JCS (1949) 933) showed that the reaction proceeded in two stages. In each of which iodine, as either iodine tribromide or iodinemonobromide might participate. Authors have examined both Price's and Robertson's experimental formulas and found some incomplete or unreasonable points. Recently it has been revealed that various halogens interact with aromatic hydrocarbons to form 1:1 complexs[4] (Keefer: JACS **73** 462 (1951) and others). Without the formation of these complexes, according to Keefer and others, readily and to a large extent as intermediates it would be difficult to explain the bromination mechanism. Iodine added to the reaction system should be regarded as a catalyst which accelerates the removal of hydrogen bromide from the complex. Authors have assumed the following reaction mechanism and obtained a new formula of reaction velocity v.

$$Br_2 + I_2 \rightleftarrows 2BrI \quad \text{(fast)} \quad ①, \qquad C_6H_6 + Br_2 \rightleftarrows C_6H_6 \cdot Br_2 \quad \text{(fast)} \quad ②$$

$$C_6H_6Br_2 + mBrI \longrightarrow C_6H_5 \cdot Br + HBr + mBrI \quad \text{(slow)} \quad ③$$

$$v = M\left[\frac{X^2}{X+Y} + \frac{LX^2Y^2}{K_1(X+Y)^3}\right]\left[\frac{XY}{X+Y} - \frac{LX^2Y^2}{K_1(X+Y)^3}\right]^m$$

where X and Y are the titers of bromide and iodine; M, L and m are constants; and K_1 is the equilibrium constant of the reaction ①. When benzene was used as a reactant, it was found that m was equal to three. This new formula has proved to hold good for various experimental results. Detailed discussion as well as results of measurement on toluene which is in progress at the author's laboratory will soon be contributed to JACS.

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