

excessively increased and subsequently the Si-H bond is electrostatically strengthened.

In the case of HCl catalyst, the reaction proceeds by the similar mechanism, but the basicity of reagent which attacks Si atom is weaker than that of OH⁻, so, for the cleavage of Si-H bond the additional attack of alcoxonium ion on H atom in this bond is required. Consequently, the order of this reaction approaches to the second order with respect to the concentration of catalyst and the reactivity of silane is also affected by the strength of its Si-H bond. Thus, the effect of substituent on the rate is more complicated since the rate is affected by two factors mutually counteracting.

Now, it is deduced from above arguments that even in the case of acid catalyst, by using of more basic anion in place of Cl⁻, the rate of cleavage is promoted and the order of its rate falls to the first order as to the catalyst as in the case of KOH.

In fact, this deduction coincides with the results observed qualitatively for the HBr catalyst in dioxane, that is, in this case the rate was markedly faster than in HCl, and of the 0.98 th order as to HBr.

13. Iodine Catalyzed Aromatic Bromination. (II)

Bromination of Toluene

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In the preceding papers (This Bulletin, 28, 71 (1952) ; *J. Am. Chem. Soc.*, 74, 5995 (1952)), it was shown that the iodine catalyzed aromatic bromination proceeds according to the following rate laws

$$v = k[ArH][Br_2][BrI]^m \quad (1)$$

$$v = Mvw^m \quad (2)$$

$$\text{or } \log(v/u) = \log M + m \log w \quad (3)$$

where u and w are functions expressed in terms of the titers of halogen, and k , M and m are constants. With benzene as reactant, m was proved to be equal to 3.

This paper presents the results obtained from several series of experiments in which the rates of bromination of toluene in carbon tetrachloride were measured in the dark at 25°.

1. Determination of the Reaction Order (m) of Iodine Bromide.

Inserting the values obtained from the measurements into equation (3), a straight line relationship between $\log(v/u)$ and $\log w$ was ascertained, its slope being equal to 3 in this case too. Further calculation shows

$$M = (22.9 \pm 3.02) \times 10^{10} \text{ [1/(moles/ml.)min.]}$$

2. Maximum Point of the Reaction Rate.

The optimum relative titer of iodine with respect to bromine was expressed as follows :

$$Y = [\{4\alpha\beta/(K_1\gamma^2)\} \{m^2/(m+1)\} + \{(m/m+1)\}]X \quad (4)$$

where X and Y are the titers of bromine and iodine, and K_1, α, β and γ are constants. With toluene as reactant, since m is equal to 3, equation (4) is transformed to equation (5) in just the same way as with benzene.

$$Y = [\{4\alpha\beta/(K_1\gamma^2)\}(9/4) + (3/4)]X \quad (5)$$

Equation (5) suggests the optimum ratio of iodine to bromine is approximately equal to 3/4, because the first term is negligibly small compared with the second. This relation was ascertained experimentally.

3. Induction Period

An induction period was found in the bromination. Examinations have revealed that the induction period becomes longer, (a) the lower the concentrations of halogens, (b) the less polar the solvent, and (c) the less reactive the hydrocarbon. Thus the induction period is not appreciable for the brominations with halogen in higher concentration (Bruner), or with reactive mesitylene as reactant (Robertson), or with toluene in chloroform (the present authors). Furthermore, the induction period was not affected by the addition of benzoyl peroxide or molecular oxygen.

From the above examinations, it was reasonably assumed that this induction period is not resulted from a radical reaction, but from an ionic one. It seems the reaction proceeds through an intermediate formation, in which iodine bromide must participate. Since equation (1) can fit only the data from the reaction which has attained to a stationary state, the overall rate of the reaction will be smaller than that expected from equation (1) before the concentration of the intermediate attains to the equilibrium concentration. Thus the longer time will be required for the reactions under the conditions (a), (b) and (c). This time can presumably be interpreted as the induction period.

14. Reactivity of Acetylene in Vinylether Synthesis

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It is well-known that the rate of vinylation of alcohol is markedly affected by the structure of alcohol used, but there have not yet been available any quantitative