The Effect of Oxygen and Reduced Nickel on the Catalytic Action of Hydrogen Bromide in the Isomerization of Isostilbene into Stilbene.

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The influence of oxygen and ferromagnetic metals on the addition of hydrogen bromide or bromine to ethylenic compounds has been investigated in this laboratory.(1) The scope of investigation has been extended to other types of reactions and it has been examined whether or not the cis-trans-isomerization is influenced by the presence of oxygen and ferromagnetic metals. Nevertheless neither oxygen nor reduced nickel showed a defined accelerating effect on the isomerization of dimethyl maleate into dimethyl fumarate and of isostilbene into stilbene even in the heat (in absence of solvents).(2)

Then the authors became aware of a short communication by M. S. Kharasch, J. V. Mansfield, and F. R. Mayo.(3) They found that in the dark carefully purified isostilbene, dissolved in benzene, was not isomerized into stilbene by hydrogen bromide when the reactants were mixed either in air or in vaccum, or in the presence of antioxidants, and that the addition of a peroxide to the reaction mixture caused complete isomerization in a few minutes.

The present authors' experiments in absence of solvents resulted in part similarly to the experiments in benzene solution by the American investigators: The presence of hydrogen bromide alone did not accelerate the isomerization of isostilbene into stilbene in the dark at room temperature, but the addition of a sufficient amount of benzoyl peroxide caused complete solidification of isostilbene into stilbene in a few minutes.

Oxygen showed a similar effect on the same reaction: When dry oxygen and dry hydrogen bromide were introduced into the tube con-

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(1) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754, 798; **12** (1937), 51, 138, 173, 356, 499.

(2) B. Tamamushi and H. Akiyama observe that the isomerizations of dimethyl maleate into dimethyl fumarate and of maleic acid into fumaric acid in aqueous solution are accelerated by the presence of molecular oxygen. *Z. Elektrochem.*, **43** (1937), 156; this Bulletin, **12** (1937), 382.

(3) *J. Am. Chem. Soc.*, **59** (1937), 1155.

taining isostilbene, the latter solidified completely in a few minutes in the dark at room temperature. The American investigators state that isostilbene in benzene solution was not isomerized to stilbene by hydrogen bromide even when the reactants were mixed in air. It may be suspected that no sufficient amount of oxygen was absorbed under the conditions of their experiments or the solvent prevented oxygen from exerting its influence.

As it was found that isostilbene does not form any peroxide with oxygen in the dark and even in diffuse light, the effect of oxygen must be attributed to the action of molecular oxygen. On the other hand, from the experimental evidence so far obtained, it cannot be decided whether benzoyl peroxide is active as such or oxygen liberated by its decomposition is the real agent.

Reduced nickel, which exhibits a catalytic action similar to that of oxygen in the addition of hydrogen bromide to allyl bromide,(4) was found also to cooperate with hydrogen bromide to accelerate the isomerization of isostilbene into stilbene. However, the effect displayed by reduced nickel and hydrogen bromide was much smaller than that by oxygen and hydrogen bromide so far as the preliminary experiments indicated. Reduced nickel contained in a reaction tube was heated at 310–320° in the atmosphere of hydrogen and then in vacuum, and cooled in vacuum. The tube, after introducing hydrogen bromide, was sealed, and isostilbene contained in a side tube attached to the reaction tube was decanted on the reduced nickel. The crystals of stilbene began to appear in the course of ½–3 hours in the dark at room temperature, and finally the whole mass solidified. The change was naturally much more rapid at the temperature of the hot water bath.

Thus it has been shown that oxygen and reduced nickel exert no direct influence on the isomerization of isostilbene into stilbene, but cooperate with hydrogen bromide, which is also inactive by itself, in accelerating the isomerization. It seems very probable that in the presence of oxygen or reduced nickel hydrogen bromide is excited to an active catalyst to promote the isomerization.

In a theory advanced for explaining the influence of oxygen and ferromagnetic metals on the addition of hydrogen bromide to allyl bromide, one of the authors (Y. U.) with M. Takebayashi assumed that these active catalysts exert some physical influence on allyl bromide,(5) but they reserved the possibility that the substance which is influenced by

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(4) This Bulletin, **11** (1936), 692, 754; **12** (1937), 51.

(5) This Bulletin, **12** (1937), 54, 175.

oxygen and ferromagnetic metals might be hydrogen bromide.(6) The results recorded in the present paper suggest the possibility that hydrogen bromide is excited by oxygen or ferromagnetic metals and the excited hydrogen bromide adds rapidly to allyl bromide to give the abnormal addition product.

M. S. Kharasch and co-workers in the cited communication bring forward a hypothesis that bromine atoms are the active catalysts in the isomerization of isostilbene into stilbene, and seem to be of the opinion that bromine atoms are responsible also for the so-called peroxide effect in the addition of hydrogen bromide to unsaturated compounds.(7) However, the effect of ferromagnetic metals on the addition of hydrogen bromide to allyl bromide cannot be explained by assuming bromine atoms, because the action of ferromagnetic metals, in contrast with oxygen and peroxides, does not undergo even the slightest modification in the presence of an antioxidant.(8) Moreover, it may be difficult to introduce a similar idea into the case of the addition of bromine to cinnamic acid in carbon tetrachloride, where oxygen retards the rate of addition while peroxides accelerate the reaction and hydrogen bromide is indifferent either in presence or in absence of oxygen.(9)

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(6) This Bulletin, **12** (1937), 176.

(7) They state the hypothesis is proposed in an article in press, but the article is not yet available here.

(8) This Bulletin, **11** (1936), 754.

(9) This Bulletin, **12** (1937), 356, 499.