The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. VI. The Homogeneity of the Catalytic Action of Oxygen. A Theory of the Oxygen Effect.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

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While in the absence of oxygen hydrogen bromide adds slowly to allyl bromide (free from peroxides) to give mainly 1,2-dibromopropane (the normal addition), in the presence of oxygen the addition is rapid and the product consists mainly of 1,3-dibromopropane (the abnormal addition). In last paper of this series[1] the authors established that the oxygen effect is caused by molecular oxygen, and pointed out that the next problem was to decide whether the catalytic action of oxygen is homogeneous or heterogeneous.

Kharasch and Mayo[2] observed that the addition of hydrogen bromide to allyl bromide is not influenced by the presence of broken glass pieces and glass wool, showing the reaction is homogeneous. The present authors have confirmed the homogeneity of this reaction by repeating similar experiments.

The ferro-magnetic metals influencing the addition of hydrogen bromide to allyl bromide similarly to oxygen are obviously heterogenous catalysts, because they remain undissolved and unchanged after reaction.

To see whether the active catalyst is dissolved oxygen or adsorbed oxygen the following experiments were carried out. Two Pyrex tubes (capacity about 140 c.c., inner surface area about 280 sq. cm.), one containing a few thin Pyrex tubes with a total surface measuring about 110 sq. cm., were charged each with 24 g. of allyl bromide and 20 g. of hydrogen bromide and 1.5 c.c. of oxygen was admitted at sealing after evacuation. The tubes were placed in the dark at room temperature for three days. They were not shaken but moved now and then. The two additions were effected simultaneously. The total yields of addition (41% for smaller surface area and 43% for greater surface area) and the compositions of the products (1,3-dibromopropane 95% for both) were the same. If oxygen adsorbed on the wall were the active catalyst, a greater

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(2) *J. Am. Chem. Soc.*, **55** (1933), 2490.

yield would be expected for the greater surface area in contact with the reacting liquid. But the two experiments resulted similar, thus demonstrating that dissolved oxygen is the active catalyst.

In this way the catalysis by oxygen has been shown to be homogeneous. As recorded in the fifth paper[1], when the amount of oxygen is 1.5 c.c. for 24 g. of allyl bromide and 20 g. of hydrogen bromide in the reaction tube with a capacity 135–140 c.c., the proportion of 1,3-dibromopropane in the product reaches 95%, and any further increase in the amount of oxygen causes no more change in the composition of the product. Even under the assumption that all the oxygen admitted were dissolved in the liquid, 1.5 c.c. correspond to only one molecule of oxygen against 3000 molecules of allyl bromide. How can such a comparatively small amount of oxygen influence so radically the addition of hydrogen bromide to allyl bromide?

The simplest explanation of the oxygen effect might be that oxygen would accelerate the abnormal addition only, say by means of chemical intervention, the normal addition being uninfluenced but conditioned only by the concentrations of the reacting substances. But then it is difficult to reconcile the following findings: The total yield obtained with 1.5 c.c. of oxygen admitted is not more than two to three times that in vacuum in three days' reaction, and in vacuum more than 90% of the product is 1,2-dibromopropane, while, in the presence of oxygen, as much as 95% is 1,3-dibromopropane, although the normal and the abnormal additions might be considered to proceed simultaneously with not very different velocities. Further the proportion of 1,3-dibromopropane should approach asymptotically a certain value as the amount of oxygen increases, whereas the curves obtained are of a quite different type (see the figures of the fifth paper). Moreover, such an explanation can not be compatible with the fact that the total yield of addition increases with the amount of oxygen admitted even after the proportion of 1,3-dibromopropane has reached the constant maximal value (95%): The absolute yield of 1,2-dibromopropane decreases rapidly as the amount of oxygen increases until the latter reaches 1.5 c.c. and thence increases in the same rate as that of 1,3-dibromopropane.

The assumption of a double action of inhibiting the normal addition and accelerating the abnormal addition is none the less inconsistent with the fact, inasmuch as the yield of 1,2-dibromopropane does not keep on decreasing as oxygen increases.

The relation between the amount of oxygen present and the result of addition can be understood if the addition catalysed by oxygen yields

95% 1,3-dibromopropane and 5% 1,2-dibromopropane and in the presence of a sufficient amount of oxygen (1.5 c.c. under the conditions of the experiments) the catalysed addition only takes place.

Thus the authors have been led to advance a theory on the oxygen effect. It is assumed that the oxygen molecule exerts some physical influence on a great number (at least 3000) of molecules of allyl bromide around it. The oxygen molecule may possess a considerably large sphere of influence capable of holding more than 3000 molecules of allyl bromide and a corresponding number of molecules of hydrogen bromide. Otherwise it may influence molecules of allyl bromide colliding with, or coming near to, it, the influenced molecules of allyl bromide keeping their influenced state for a considerably long period—there exist always more than 3000 influenced molecules of allyl bromide per one molecule of oxygen. If allyl bromide has been influenced at all by oxygen in either way, hydrogen bromide adds rapidly to it, 95% of the influenced allyl bromide being transformed into 1,3-dibromopropane and 5% into 1,2-dibromopropane, and thus both dibromopropanes being formed from the influenced molecules of allyl bromide in the presence of a sufficient amount of oxygen. The strength or the freshness of the oxygen influence affects only the rate of addition.

The theory explains satisfactorily the results recorded in the fifth paper: When about 1.5 c.c. of oxygen is admitted under the conditions of the experiments, the whole liquid is just filled with such spheres of influence or all the molecules of allyl bromide exist in the influenced state, and the proportion of 1,3-dibromopropane in the product is 95%. An increase in the amount of oxygen augments the strength or the freshness of the oxygen influence, and an increase in the total yield of the addition is obtained without any further appreciable change in the composition of the product.

It may be considered that the effect of the ferro-magnetic metals is caused by a similar influence. That the normal addition is far inhibited by the presence of these heterogeneous catalysts can not be explained except by the above-mentioned theory. But, the metals are very coarsely divided compared with the dissolved oxygen, and, therefore, their influence must be very strong compared with that of oxygen, corresponding to a very large sphere of influence or to a very long preservation of the influenced state on the part of allyl bromide.

The influence exerted by oxygen and the ferro-magnetic metals is considered to be related closely to the great magnetic susceptibilities with which these substances are endowed. What change occurs in the molecule

of allyl bromide under the influence of oxygen and the ferro-magnetic metals is unknown, but it can be said that the ordinary form preferring the normal addition is changed into an extraordinary form preferring the abnormal addition.

The theory advanced by the authors explains satisfactorily the effect of oxygen and the ferro-magnetic metals on the addition of hydrogen bromide to allyl bromide. Nevertheless, it may be open to question that the authors have taken it for granted that oxygen and the ferro-magnetic metals have nothing to do with hydrogen bromide, because hydrogen bromide could take the place of allyl bromide in the theory stated above. Further experiments are required before it can be decided whether the substance to be influenced by oxygen and the ferro-magnetic metals is allyl bromide or hydrogen bromide.

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Chemical Institute, Faculty of Science,
Imperial University of Tokyo.