The Mechanism of the Oxygen Effect on Hydrogen Bromide Reacting with Ethenoid Compounds.

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Introduction.(1) In 1933, at the Dyson Perrins Laboratory, Oxford, one (Y.U.) of the authors had occasion to prepare 11-bromoundecanoic acid by adding hydrogen bromide to undecenoic acid according to the work by Walker and Lumsden.(2) Undecenoic acid was dissolved in toluene, a portion of toluene was distilled off to remove moisture, and hydrogen bromide was passed immediately into the cooled solution, when 10-bromoundecanoic acid was found to be the main product. On the other hand, when undecenoic acid was dissolved in toluene, both after being dried separately, and without distillation of the solvent hydrogen bromide was passed into the solution, the product was 11-bromoundecanoic acid. At that time it was assumed that the difference was caused by traces of moisture entering when the solution was prepared.(3)

Kharasch and Mayo(4) soon found that hydrogen bromide adds to pure allyl bromide in the absence of oxygen to give mainly 1,2-dibromopropane (normal reaction) while in the presence of peroxides or oxygen 1,3-dibromopropane is the main product (abnormal reaction). The effect was attributed to the action of peroxides and called "peroxide effect." The effect can be eliminated by the addition of antioxidants, e.g. diphenylamine and hydroquinone. Later Urushibara and Takebayashi(5)(6) showed that the effect of oxygen is caused by the action of molecular oxygen and suggested the possibility that the effect of peroxides might be due to the action of molecular oxygen generated by the decomposition of the peroxides. Further it was demonstrated that the abnormal reaction caused by oxygen is homogeneous.(7)

Ashton and Smith(8) studied the addition of hydrogen bromide to undecenoic acid in the light of Kharasch's observations and found that oxygen is the agent reversing the direction of addition also in this case.

Urushibara and Takebayashi,(9) studying the effects of various substances other than oxygen and peroxides, observed that ferromagnetic metals such as reduced nickel and reduced iron influence the addition of hydrogen bromide to allyl bromide quite in the same way as oxygen. Reduced nickel was found effective also in reversing the direction of

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(1) Compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461.

(2) J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **79** (1901), 1191.

(3) Comare *Chemistry and Industry*, **52** (1933), 219.

(4) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

(5) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 798.

(6) *Idem, ibid.*, **12** (1937), 138.

(7) *Idem, ibid.*, **12** (1937), 173.

(8) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.

(9) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51; **13** (1938), 400.

addition of hydrogen bromide to undecenoic acid in toluene solution.(10) While diphenylamine hardly affects the influence of reduced nickel and reduced iron, hydroquinone and catechol inhibit the action of reduced nickel to a great extent.(12)(13) Reduced nickel and reduced iron are stable to hydrogen bromide under the conditions of the experiments, while reduced cobalt is so liable to attack by hydrogen bromide that the effect of the metal is only moderately displayed.(11)(14)

The peculiar influence of oxygen and the ferromagnetic catalysts on hydrogen bromide has been observed further in the isomerization of isostilbene to stilbene, a reaction apparently quite different from the addition reactions. Kharasch and co-workers(15) found that in the dark pure isostilbene, dissolved in benzene, is not isomerized to stilbene by hydrogen bromide alone, but the addition of a peroxide to the mixture causes complete isomerization in a few minutes. The present authors(16)(17) extended Kharasch's observation to oxygen and to the ferromagnetic catalysts, viz., reduced nickel and reduced iron. Isostilbene, in the pure liquid state or in benzene solution, is isomerized to stilbene by hydrogen bromide in the presence of oxygen in the dark at room temperature. Reduced nickel and reduced iron also co-operate with hydrogen bromide to isomerize isostilbene, although the effect of hydrogen bromide in the presence of the ferromagnetic catalysts is much smaller than in the presence of oxygen under the conditions of the experiments. The strengths of the inhibiting actions of diphenylamine and catechol on oxygen and reduced nickel are quite parallel to those displayed in the cases of the addition reactions.(17)

A theory on the mechanism of the effect of oxygen or peroxides as outlined above have been presented by Kharasch and co-workers.(15)(18) The cis-trans isomerization caused by bromine and light is attributed to the action of bromine atoms.(19) Isostilbene is isomerized by hydrogen bromide not only in the presence of peroxides but also in sunlight, and hydroquinone inhibits the isomerization in either case.(15) Further the transformation of ethyl α-bromoacetoacetate into ethyl γ-bromoacetoacetate by hydrogen bromide is accelerated by peroxides or oxygen as well as by light.(20) Kharasch assumes that bromine atoms are formed from hydrogen bromide by the action of peroxides or oxygen just as by the action of light and cause such effects. The effect of peroxides and oxygen on the addition of hydrogen bromide to ethenoid compounds was also explained on the assumption of bromine atoms.(18) Thus, the mechanism of the addition of hydrogen bromide to vinyl bromide, which was originally represented by electronic formulæ, may be put into ordinary formulæ as

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(10) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331, 404, 574.
(11) *Idem, ibid.*, **11** (1936), 754.
(12) *Idem, ibid.*, **13** (1938), 400.
(13) *Idem, ibid.*, **13** (1938), 404.
(14) *Idem, ibid.*, **12** (1937), 51.
(15) M. S. Kharasch, J. V. Mansfield, and F. R. Mayo, *J. Am. Chem Soc.*, **59** (1937), 1155.
(16) Y. Urushibara and O. Simamura, this Bulletin, **12** 1937), 507.
(17) *Idem, ibid.*, **13** (1938), 566.
(18) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 288.
(19) A. Berthoud and Ch. Urech, *J. Chim. Phys.*, **27** (1930), 291.
(20) M. S. Kharasch, E. Sternfeld, and F. R. Mayo, *J. Am. Chem. Soc.*, **59** (1937), 1655.

follows:

$$\mathrm{BrCH{=}CH_2 + HBr \rightarrow Br_2CH{-}CH_3} \quad \text{(normal reaction)}$$

$$\mathrm{HBr + O_2} \text{ (or peroxides) } \xrightarrow{\mathrm{CH_2{=}CHBr}} \mathrm{HO_2 + Br}$$

$$\mathrm{BrCH{=}CH_2 + Br \rightarrow Br\underset{|}{C}H{-}CH_2Br}$$

$$\mathrm{Br\underset{|}{C}H{-}CH_2Br + HBr \rightarrow BrCH_2{-}CH_2Br + Br}\,.$$

The essential features of these representations are that in the normal reaction the bromide ion is directed toward the carbon atom with the lowest electron density to yield 1,1-dibromoethane, and that in the abnormal reaction the bromine atom is directed toward the carbon atom with the greater electron density to yield a 1,2-dibromoethyl free redical. This free radical then reacts with hydrogen bromide to yield 1,2-dibromoethane and another bromine atom, which is responsible for the propagation of the chain reaction. According to this mechanism the function of peroxides or oxygen is to produce bromine atoms acting as chain carriers.

Hey and Waters(21) also suggested that the addition process of the abnormal reaction is one requiring the transient production of neutral atoms of hydrogen and bromine from hydrogen bromide.

Winstein and Lucas,(22) to explain the directive influence of oxygen in the abnormal additions of hydrogen bromide to the double bonds, assumed the formation of an oxygen complex from the unsaturated molecule prior to the addition of hydrogen bromide. It will be, however, soon self-evident that this theory cannot explain the experimental facts.

Urushibara and Takebayashi(14)(6) also considered previously the mechanisms of the effects of oxygen and reduced nickel on the addition of hydrogen bromide to allyl bromide. The simplest explanation of the oxygen effect might be that the two reactions, one giving 1,2-dibromopropane and the other 1,3-dibromopropane, were simultaneous reactions proceeding without interfering with each other but with respective velocities determined by the concentrations of the reactants, oxygen accelerating the latter reaction only but being indifferent to the former. Such a simple explanation encounters at once serious difficulties. In the absence of oxygen 95% of the product is 1,2-dibromopropane. In the presence of oxygen 95% is 1,3-dibromopropane, while the total yield is not more than threefold in three days reaction. Assume that the two reactions were simultaneous reactions of the second order, then the following relations would exist:

$$x = y+z\,,$$

$$\frac{dy}{dt} = k_1(a-x)(b-x)\,,$$

$$\frac{dz}{dt} = k_2(a-x)(b-x)\,,$$

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(21) D. H. Hey and W. A. Waters, *Chem. Rev.*, **21** (1937), 202.

(22) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60** (1938), 836.

$$\frac{dx}{dt} = (k_1+k_2)(a-x)(b-x) \qquad (1),$$

$$\frac{y}{z} = \frac{k_1}{k_2} \qquad (2),$$

where a and b represent the initial amounts of allyl bromide and hydrogen bromide respectively, x the amount of allyl bromide which reacts in time t, y and z the amounts of 1,2- and 1,3-dibromopropanes formed in time t respectively, and k_1 and k_2 constants. The above simple explanation requires only an increase of k_2 to k_2' in the presence of oxygen. The ratio $(k_1 + k_2')/(k_1 + k_2)$ can be evaluated from (1) and from (2) independently: Inserting the values obtained in the experiments,(5) values 3.3–5.4 are obtained from the relation (1) of the total reaction velocity while 19–22 from the relation (2) of the composition of the reaction product.

In the cases of vinyl bromide(23) and vinyl chloride(24) the reversal of the direction of addition by oxygen is more conspicuous: In the absence of oxygen the product is 100% ethylidene dihalide while in the presence of oxygen 100% ethylene dihalide. The fact that the normal reaction does not occur at all in the presence of oxygen cannot be explained on the assumption of the mere acceleration of the abnormal reaction by oxygen. Another difficulty is that the total yield of the products from allyl bromide and hydrogen bromide increases with the amount of oxygen admitted even after the proportion of 1,3-dibromopropane has reached the constant maximal value (95%); that is to say, the absolute yield of 1,2-dibromopropane decreases rapidly as the amount of oxygen increases until the latter reaches a certain amount and thence increases in the same rate as that of 1,3-dibromopropane.(5)

Smith(25) has briefly reported that the normal reaction of undecenoic acid and hydrogen bromide with thorough elimination of oxygen proceeded with a rate less than one-fiftieth of the speed of the abnormal reaction. It suffices, however, to point out that allyl bromide and hydrogen bromide give a product containing 95% 1,2-dibromopropane in a certain yield under a set of conditions and another product containing 95% 1,3-dibromopropane in a yield not more than three times as much under another set of conditions which differs from the former only in that a certain amount of oxygen is admitted. In the experiments by Urushibara and Takebayashi(10) on the addition of hydrogen bromide to undecenoic acid in toluene solution quantitative yields were always obtained regardless of the conditions and of the compositions of the products.

In the presence of reduced nickel which has never been in contact with air, allyl bromide and hydrogen bromide give a product containing 95% 1,3-dibromopropane in a total yield only twice as much as that obtained in the absence of the catalyst.(14) Reduced nickel is a heterogeneous catalyst, yet the normal reaction giving 1,2-dibromopropane is

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(23) M. S. Kharasch, M. C. McNab, and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2521.

(24) M. S. Kharasch and C. W. Hannum, *ibid.*, **56** (1934), 712.

(25) J. C. Smith, *Chemistry and Industry*, **57** (1938), 464.

inhibited throughout the reacting system, the bulk of which is not in contact with the catalyst.

Thus Urushibara and Takebayashi⁽⁶⁾ was led to assume that in the presence of a sufficient amount of oxygen (or reduced nickel) the catalyzed addition only takes place, and that the catalyzed addition yields a product consisting of 95% 1,3-dibromopropane and 5% 1,2-dibromopropane. The amount of oxygen just sufficient for producing the maximal proportion (95%) of 1,3-dibromopropane is 1.5 c.c. (n.p.t.) for 24 g. allyl bromide and 20 g. hydrogen bromide in a reaction vessel of 140 c.c. capacity.(5) Even if the whole oxygen were dissolved in the liquid, only one molecule of oxygen would be available for 3,000 molecules of allyl bromide. From a very fascinating speculation that the actions of oxygen and reduced nickel might be connected with their magnetic properties, it was assumed that each molecule of oxygen would exert some physical influence over at least 3,000 molecules of allyl bromide.

If the direction of addition of hydrogen bormide were decided according to the polarity of the allyl bromide molecule, how could one molecule of oxygen reverse totally the polarity of so many molecules of allyl bromide? Although it has been made probable that the substance to be influenced by oxygen and reduced nickel is hydrogen bromide,(16) it is non the less difficult to understand how one molecule of oxygen could exert a physical influence on thousands of molecules of hydrogen bromide. Thus the assumption of a chain mechanism seems necessary as in the case of a photochemical reaction with a great quantum yield.

Although Kharasch's theory of the chain reaction involving bromine atoms has obtained nearly no experimental evidence except an analogy with the photochemical reactions, no objection can be raised from the experimental results obtained by Urushibara and co-workers. On the contrary, the formation of stilbene dibromide in the experiment of isomerization of isostilbene by hydrogen bromide and oxygen in benzene solution seemed to favour Kharasch's theory.(17) Considering the very close resemblance of the effects of oxygen and reduced nickel, it may be presumed that the essential parts of the mechanisms of their actions are the same; yet there have been obtained no bases nor analogies to postulate the formation of bromine atoms from hydrogen bromide and reduced nickel. Thus the present authors have been led to carry out the experiments described below and elsewhere to discuss on Kharasch's theory on the one hand and to know the mechanism of the action of reduced nickel on the other, and, as for the mechanism of the oxygen effect, not only Kharasch's theory has been substantiated in principle but also a more comprehensive treatment of the matter has been made on the basis of the experimental results.

Action of Hydrogen Bromide and Oxygen on Catechol. As it seemed that the antioxidants would afford a clue to elucidation of the mechanism of the oxygen effect, the behaviour of catechol, the most effective of the antioxidants used in this laboratory, towards oxygen and hydrogen bromide was examined.

To a solution of 0.5 g. of catechol in 140 g. of carbon tetrachloride (catechol remained partly undissolved) a mixture of hydrogen bromide and oxygen was passed for two hours in the dark at room temperature. No sign of change was noticeable and from the reaction mixture which had stood overnight the whole amount of catechol was recovered unchanged. Thus it was demonstrated that hydrogen bromide and oxygen do not unconditionally (or even in the presence of catechol) produce atoms or molecules of bromine. As it was then anticipated that the presence of an unsaturated compound might be essential for the formation of bromine atoms from hydrogen bromide and oxygen, the following experiments were carried out.

Action of Hydrogen Bromide and Oxygen on Allyl Bromide. Hydrogen bromide and oxygen do not react at room temperature as shown by the above experiment. Further it was previously observed that no peroxide was produced from allyl bromide and oxygen in the dark, but diffuse light caused the formation of a peroxide in a few days.(4)

Commercial allyl bromide was purified by washing with water and distilling in the dark, and a portion boiling at a constant temperature was used preferably immediately after distillation. Hydrogen bromide and oxygen were dried separately by passing over phosphorus pentoxide, mixed in a T-tube, and introduced into allyl bromide cooled with ice water in the dark (without cooling much heat was evolved causing the evaporation of allyl bromide). Changes were occasionally observed in dim light from an incandescent lamp. Much complicated reactions were perceived to occur during the passage of the gas mixture. There was no change in the beginning, but by and by the allyl bromide became turbid until drops of a liquid were distinctly observed on its surface. After a while it was noticed that the liquid became faintly yellow for a moment on shaking, indicating the liberation of bromine. The temporary coloration appearing on shaking grew deeper gradually but disappeared at once. Finally the coloration due to bromine persisted, but the liberation of bromine was not carried on beyond a certain extent on continuing the passage of the gas mixture.

The weight of the reaction products corresponded nearly to the amount expected from the addition of hydrogen bromide to allyl bromide, if it was taken into account that part of allyl bromide might have been carried away with the gas mixture. The liquid which separated on the surface was recognized as water. The colourless reaction mixture set free iodine from aqueous potassium iodide acidified with hydrochloric acid, showing that a peroxide had been formed in the reaction. The peroxide, however, is fairly stable and does not decompose easily, and the liberation of iodine from the iodide solution was not completed even when heat was applied. When the reaction mixture was shaken with water, the peroxide was found to shift partly to the aqueous layer as was shown by the liberation of iodine from the iodide solution. The liberation of iodine, however, was very slowly brought to completion even in the aqueous solution. Owing to such stability of the peroxide it was difficult to determine exactly its amount by titrating liberated iodine with a standard thiosulphate solution, but it was roughly estimated that the amount of the peroxide corresponded to 0.1 to 0.2 g. atom of iodine per 1 mole of allyl bromide used. The formation of the peroxide was detected even after a few minutes' action of the gas mixture.

When the reaction mixture was washed with water, dried, and distilled under the atmospheric pressure, vigorous decomposition of the peroxide set in and hydrogen bromide was evolved. No fractions corresponding to allyl bromide and 1,2-dibromopropane were obtained and the temperature of the vapour rose abruptly, the greater part distilling near the boiling point (165°) of 1,3-dibromopropane. A fraction distilling above 200° was obtained in an amount corresponding to less than one-tenth of the whole products and a small amount of a carbonized matter remained in the flask. Thus 1,3-dibromopropane was found to form the greater part of the whole products.

As already mentioned, there occurs no change between allyl bromide and oxygen on the one hand and between hydrogen bromide and oxygen on the other. When hydrogen bromide was passed into allyl bromide in the same apparatus as used in the above experiment 1,3-dibromopropane was formed almost quantitatively (air being not excluded, the abnormal reaction took place), but neither water nor peroxide was produced. It is only when all three of allyl bromide, hydrogen bromide and oxygen are present that the reactions as described above take place.

Water seems to have been yielded from hydrogen peroxide which may have been primarily formed. The reasons are as follows: In general the first stage of the oxidation by molecular oxygen is the formation of peroxides. On passing hydrogen bromide and oxygen into allyl bromide a certain amount of bromine liberated remained unconsumed, thus suggesting that the oxidation of hydrogen bromide to bromine occurred to some extent even after the whole allyl bromide had reacted. Inasmuch as the organic peroxide is stable in the presence of much hydrogen bromide as mentioned above it could not be the oxidizing agent. The direct oxidation of hydrogen bromide by oxygen having been ruled out, the only remaining alternative is that the formation of water and bromine is caused by the action of hydrogen peroxide primarily formed on hydrogen bromide.

The bromine thus formed must enter into reaction with allyl bromide, yielding 1,2,3-tribromopropane (b.p. 219–221°), which may have been contained in the fraction boiling above 200°. In a separate experiment 1,2,3-tribromopropane was prepared by adding bromine to allyl bromide and was found not to liberate iodine from aqueous potassium iodide acidified with hydrochloric acid.

It has been established by Bockemüller and Pfeuffer(26) that the simultaneous action of bromine and oxygen on allyl bromide gives a peroxide $(BrCH_2)_2CH\text{-}O\text{-}O\text{-}CH(CH_2Br)_2$ besides the tribromopropane. In the present case a part of the peroxide may have been resulted from allyl bromide, oxygen and the secondarily formed bromine by the same process as in the German investigators'; but that this is of subordinate importance is obvious on the following ground. Though the experiments by Bockemüller and Pfeuffer were performed under the conditions most favourable to the action of oxygen, the molar ratio of the oxygen consumed to the bromine which reacted was found as 1:6.5 (25°), corre-

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(26) W. Bockemüller and L. Pfeuffer, *Ann.*, **537** (1939), 178

sponding to the formation of less than one mole of the peroxide while five moles of the tribromopropane were produced. It was manifest in the present experiments that five times as much tribromopropane as the peroxide (as much as 0.4 mole of the tribromopropane for one mole of allyl bromide) and the corresponding amount of water (0.5 mole from one mole of allyl bromide) were not formed. In an experiment with 0.4 mole of allyl bromide the amount of water formed was estimated with the eye to amount only to a few tenths of 1 c.c.; and less than ten per cent of the whole products distilled near the boiling point of 1,2,3-tribromopropane. Hence, it must be concluded that the peroxide obtained in the present case was produced at least for the most part by the direct action of allyl bromide, oxygen and hydrogen bromide.

Action of Hydrogen Bromide and Oxygen on Stilbene. It has already been mentioned that in the isomerization of isostilbene by hydrogen bromide and oxygen in benzene solution a small amount of stilbene dibromide was formed.(17) To examine the action of hydrogen bromide and oxygen upon stilbene the gas mixture was passed into a benzene solution (50 c.c.) of stilbene (0.218 g.) under the same conditions as in the experiments with allyl bromide. After about fifteen minutes' passage of the gas mixture it was noticed that the solution had become yellow with bromine, and the coloration did neither fade on shaking nor become deeper on continuing the passage of the gas mixture. The gas was passed further for five minutes. When a sample from the reaction mixture was added to aqueous potassium iodide iodine was liberated and the benzene layer became violet. When the reaction mixture was evaporated in vacuum at room temperature there remained fine crystals embedded in an orange-coloured oil having an aromatic odour. The whole products weighed 0.433 g., while if all the stilbene used was to be converted into the dibromide it should give 0.412 g. A small volume of benzene was added to the mass and the crystalline substance was collected on a sheet of filter paper. It melted at 238° with decomposition and was identified as stilbene dibromide by the melting point of a mixture with an authentic specimen. The benzene extract contained a small amount of a peroxide as indicated by the test with ferrous ammonium sulphate and ammonium thiocyanate. The nature of the oily product was not further pursued.

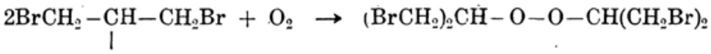
As a control experiment the gas mixture was passed into pure benzene (50 c.c.) for 25 minutes, but neither any coloration of the liquid nor the liberation of iodine on shaking the benzene with the iodide solution was observed.

The Mechanisms of the Reactions of Hydrogen Bromide, Oxygen and the Ethenoid Compounds as well as the Mechanism of the Abnormal Addition in the Presence of Oxygen. On the basis of the experimental results and the interpretation of them described above, the reactions in question seem to be represented by the schemes as shown below for the case of allyl bromide. The oxidation of hydrogen bromide by oxygen takes place with allyl bromide as a necessary acceptor of bromine atoms, giving rise to hydrogen peroxide and a dibromoisopropyl radical:

$$2\mathrm{CH_2{=}CH{-}CH_2Br} + 2\mathrm{HBr} + \mathrm{O_2} \longrightarrow 2\mathrm{BrCH_2{-}}\underset{|}{\mathrm{CH}}\mathrm{{-}CH_2Br} + \mathrm{H_2O_2}\,.$$

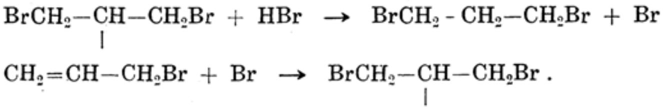
Here the diradical nature of oxygen comes into play, and the production of hydrogen peroxide may probably be preceded by the intermediate formation of a radical HO_2. Thus the above process may have to be further resolved into steps. An expression such as $2HBr + O_2 \rightarrow 2Br + H_2O_2$, however, should be avoided, because it is to be emphasized that the oxidation of hydrogen bromide by oxygen is only possible in the presence of an ethenoid compound.

Then the organic peroxide forms itself with all probability from the dibromoisopropyl radical and oxygen, and thus may be identical with that formed in the reaction of Bockemüller and Pfeuffer:



$$2BrCH_2-\underset{|}{C}H-CH_2Br + O_2 \rightarrow (BrCH_2)_2CH-O-O-CH(CH_2Br)_2 .$$

Even in the presence of much oxygen the greater part, and in the presence of a small amount of oxygen almost all, of the dibromoisopropyl radical starts the following chain reaction:



$$BrCH_2-\underset{|}{C}H-CH_2Br + HBr \rightarrow BrCH_2-CH_2-CH_2Br + Br$$

$$CH_2=CH-CH_2Br + Br \rightarrow BrCH_2-\underset{|}{C}H-CH_2Br .$$

The abnormal additions of hydrogen bromide to ethenoid compounds can be considered to proceed by such chain processes.

The hydrogen peroxide oxidizes hydrogen bromide to produce bromine and water:

$$H_2O_2 + 2HBr \rightarrow 2H_2O + Br_2 ,$$

and the bromine set free adds probably for the most part to allyl bromide to yield 1,2,3-tribromopropane:

$$CH_2=CH-CH_2Br + Br_2 \rightarrow BrCH_2-CHBr-CH_2Br .$$

It may also be possible that the tribromopropane results from the addition of a second bromine atom to the dibromoisopropyl radical.

Inasmuch as the radicals and some of the compounds taking part in the above mechanism are to be considered as very reactive, there may be many other possibilities of reactions among them. For the sake of simplicity, however, only those processes that are necesary to explain what has been observed are considered. Minor particulars cannot be decided from the results so far obtained.

In the case of stilbene, the reaction seems to follow a course like the above in the main, but stilbene dibromide is the main product in this case and seems to be formed for the most part by the addition of two atoms of bromine in two steps.

The inhibiting action of the antioxidants on the abnormal addition reactions is considered to consist in capturing bromine atoms, thus interrupting the propagation of chains.

That the molecular bromine does not accelerate the abnormal addition has been shown by Smith.(27) In the addition of hydrogen bromide

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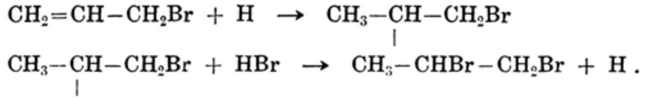
(27) J. C. Smith, *Chemistry and Industry*, **57** (1938), 465.

to undecenoic acid in dilute benzene solution, thé addition of much bromine caused the abnormal addition, but the necessary amount was very large compared with that of oxygen which was efficient enough in traces. In a concentrated solution hydrogen bromide added normally although bromine was consumed.

Thus not only Kharasch's hypothesis has been experimentally substantiated and it has been established that hydrogen bromide and oxygen give rise to bromine atoms in the presence of ethenoid compounds, but also the fate of hydrogen atoms and the reactions to proceed in the presence of much oxygen have been made clear.

The Mechanism of the Normal Addition. Since the double bond at the end of a chain, and especially the terminal unsaturated carbon atom, are associated with the least steric hindrance, it can be anticipated from a steric point of view that addition will take place at this carbon atom with the greatest ease. Thus, if hydrogen bromide adds by atoms, the atom adding first to the double bond, whether it may be the bromine atom or the hydrogen atom, will prefer the terminal position. No contradiction is tenable from the consideration of the electron density, because the atom, whether bromine or hydrogen, will be directed toward the terminal carbon atom with the greater electron density and it is hardly possible that the electron density should be affected by oxygen. If the initiative in addition, hence the terminal position, is taken exclusively by the bromine atom or by the hydrogen atom, then the product will contain a predominating proportion of either of the two isomerides. In the addition of hydrogen bromide to ethenoid compounds with terminal double bonds, e.g. allyl bromide and vinyl bromide, the products obtained under extreme conditions consist mainly or solely of either of the two possible isomerides. It must be noted here that in the above-mentioned examples oxygen exactly reverses the proportion of the two isomerides. An inspection of the constitutions of the main or sole products indicates at once that the initiative in addition is taken by the hydrogen atom in the normal reaction and by the bromine atom in the abnormal reaction. The abnormal reaction taking place in the presence of oxygen has just been explained on the basis of a chain mechanism involving the bromine atom and the radical formed by the addition of the bromine atom to the terminal carbon atom of the unsaturated molecule. The fact that the normal reaction is inhibited totally as the abnormal one becomes active, is well understood on the assumption that the normal reaction is also a chain reaction (see below). Thus the normal reaction may be represented by the following scheme:



$$\mathrm{CH_2{=}CH{-}CH_2Br} + \mathrm{H} \rightarrow \mathrm{CH_3{-}\underset{|}{C}H{-}CH_2Br}$$

$$\mathrm{CH_3{-}\underset{|}{C}H{-}CH_2Br} + \mathrm{HBr} \rightarrow \mathrm{CH_3{-}CHBr{-}CH_2Br} + \mathrm{H}\,.$$

Even in the presence of a sufficient amount of oxygen about 5% of the product from allyl bromide and hydrogen bromide is 1,2-dibromopropane, while in the absence of oxygen 1,3-dibromopropane is formed in a proportion of about 5%. Thus it can be assumed that about one-twentieth of the atoms, either bromine or hydrogen, taking the initiative in addition add to the carbon atoms adjacent to the terminal carbon atoms rather than that the atoms adding first are all directed to the terminal carbon atoms and consist of 95% of one and 5% of the other, because in the cases of vinyl halides it must be concluded that all the atoms taking the initiative in addition are either bromine atoms or hydrogen atoms and add exclusively to the terminal carbon atoms, indicating that the compositions of the products obtained under extreme conditions depend entirely on the nature of the unsaturated molecules.

The accelerating effect of platinum black on the normal reaction may be attributed to the activation of the hydrogen atom of hydrogen bromide which takes the initiative in addition. The following facts support this idea: (1) While reduced nickel does not act as a hydrogenating catalyst at ordinary temperature, platinum black can activate hydrogen at ordinary temperature and pressure. (2) If hydrogen bromide is added to allyl bromide in the presence of both platinum black and oxygen, the composition of the product is intermediate and in this case bromine is liberated and remains free in spite of the presence of allyl bromide unchanged.(4) This may be interpreted as that the hydrogen atom activated by platinum black combines partly with oxygen while the unpaired bromine atom cannot add even to the unsaturated allyl bromide and is thrown off temporarily as a bromine molecule.

Since it seems that the normal reaction, or strictly speaking the reaction giving the same product as the normal reaction, accelerated by platinum black and the abnormal reaction caused by oxygen proceed side by side, the addition initiated by the hydrogen atom activated by platinum black is probably concluded by the combination of the remaining bromine atom to form 1,2-dibromopropane without commencing the chain reaction as shown above (further see below).

The Cancelling of the Normal and the Abnormal Chains. If the normal and the abnormal chains are brought into co-existence, the bromoisopropyl radical and the hydrogen atom of the former may combine with the bromine atom of the latter on the one hand, and, on the other, the dibromoisopropyl radical and the bromine atom of the abnormal chain may combine with the hydrogen atom of the normal chain. Thus cancelling of the two kinds of chains may occur and either kind remaining after this process will be propagated freely. After all the chains propagating in the system have become abnormal ones, the increase of the chains by increasing the amount of oxygen will cause only the increase of the reaction velocity without affecting the composition of the product. The experimental results are in perfect accordance with this.(5)

According to the above idea, the abnormal and the normal reactions cannot proceed side by side both in considerable intensities during a long time. Thus the fact that products of intermediate compositions are obtained under intermediate conditions needs an explanation. This affords, however, no indication that the two reactions should proceed side by side in a ratio that might be revealed by the compositions of the products. On the contrary, a simple calculation from the data obtained previously(5) makes it quite clear that under such conditions the normal chains predominate in the first stage of the reaction but are gradually supplanted by the abnormal chains.

Amount of oxygen admitted (c.c.)	Total yield (%)			1,3-Dibromopropane (%) in the product formed in		
	3 days	5 days	Diff.	3 days	5 days	Last 2 days in 5 day reaction
0*	14	24	10	4	12	23
0.5	21	37	16	38	60	89

* A minute quantity of oxygen may have possibly been present, because the evacuation of air was effected with a rotary pump.

The accompanying table shows that the normal reaction is gradually supplanted by the abnormal reaction with the lapse of time. Such a phenomenon, which may be represented by the term "induction period," must occur also within 3 days, and it goes without saying that the more oxygen is present the quicker the abnormal reaction takes the place of the normal one. Thus the intermediate composition represents only the sum of products formed in the course of such rise and fall of the two reactions, and not the proportion with which the two reactions proceed all the time.

It is not impossible that oxygen may inhibit the normal reaction by catching the hydrogen atom carrying the normal chain; however, as the normal reaction can be eliminated by a very small amount of oxygen such a mechanism may not be responsible for the formation of water (or hydrogen peroxide) in the reaction of allyl bromide, hydrogen bromide and oxygen.

The Mechanism of the Cis-trans Isomerization by Hydrogen Bromide and Oxygen. It has already been suggested that the isomerization of isostilbene to stilbene by hydrogen bromide and oxygen may be closely related with the addition of hydrogen bromide to ethenoid compounds in the presence of oxygen. Thus it may reasonably be assumed that the first stage of the isomerization is the same as that of the addition, namely, the addition of the bromine atom formed from hydrogen bromide and oxygen to produce a bromo radical. Here the second stage of addition, namely, the formation of the completed addition product and another bromine atom, does not occur owing to the small concentration of hydrogen bromide and especially to the nature of the unsaturated linkage, but the bromine atom which has entered the unsaturated molecule goes out and moves to another molecule of the unsaturated compound. Thus the mechanism is quite analogous to that of the isomerization by bromine and light. However, the addition of a bromine atom to the double bond, free rotation about the single bond thus formed and elimination of the bromine atom, as postulated by Berthoud(19)(28), do not explain the inversion of the geometrical isomerides. The addition (or the elimination)

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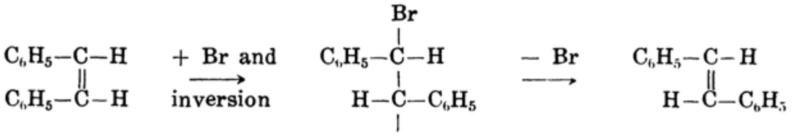
(28) Compare further D. H. Hey and W. A. Waters, *Chem. Rev.*, **21** (1937), 169 and W. A. Waters, "Physical Aspects of Organic Chemistry," 139, London (1937).

of the bromine atom should be accompanied by an inversion of either of the unsaturated carbon atoms.(29) Then the isomerization of isostilbene by hydrogen bromide and oxygen may be represented as a chain reaction shown below:



$$\begin{matrix} C_6H_5-C-H \\ \| \\ C_6H_5-C-H \end{matrix} \xrightarrow[\text{inversion}]{+\ Br\text{ and}} \begin{matrix} Br \\ | \\ C_6H_5-C-H \\ | \\ H-C-C_6H_5 \\ | \end{matrix} \xrightarrow{-\ Br} \begin{matrix} C_6H_5-C-H \\ \| \\ H-C-C_6H_5 \end{matrix}$$

The inhibiting action of antioxidants on the cis-trans isomerization by hydrogen bromide and oxygen can be attributed also to the break of the chains due to the capture of bromine atoms by them.

If much hydrogen bromide and oxygen be present, the bromo radical takes up another bromine atom to form stilbene dibromide rather than hydrogen atom from hydrogen bromide.

Cases where the Effect of Oxygen is Undetectable. It is beside the question of the present paper whether or not oxygen will affect the additions of hydrogen bromide proceeding by other mechanisms, e.g., ionic addition. The effect of oxygen, however, may be undetectable in certain cases of atomic additions by the chain mechanism.

Let the two unsaturated carbon atoms be designated as α and β. If the α carbon atom is terminal, any atom adding first will prefer it. In the case of allyl bromide 95% of the atoms adding first are directed to the α carbon atoms, while in cases of vinyl halides all the atoms adding first combine with the α carbon atoms. Here it may be pointed out again that, whether the atoms adding first are bromine or hydrogen, they are distributed between the α and β positions in the same proportion.

If the double bond is not situated at the end of a chain and the α and β carbon atoms are alike in their properties, the atoms adding first may tend to be distributed equally between the α and β carbon atoms. In such a case the product may be near to a 50%:50% mixture of two isomerides, and irrespective of the kind of the atoms adding first the result of addition may be the same if seen from the composition of the product, and, therefore, the effect of oxygen may be difficult to detect.

Thus, Smith and co-workers(30) observed that the addition of hydrogen bromide to isoundecenoic acid or to the corresponding alcohol gives a mixture containing equal amounts of two isomerides either in the presence or in the absence of oxygen. Further Kharasch and co-workers(31) added hydrogen bromide to *cis*- and *trans*-pentene-(2) and obtained equal amounts of 2-bromopentane and 3-bromopentane regardless of the conditions of addition and of the spatial configuration of pentene-(2).

The distribution of the bromine atoms adding first between the α and β carbon atoms may not always be equal to that of the hydrogen

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(29) Compare R. L. Shriner, R. Adams, and C. S. Marvel, "Gilman's Organic Chemistry," Vol. I, 378, New York (1938).

(30) P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108; E. P. Abraham, E. L. R. Mowat, and J. C. Smith, *ibid.*, **1937**, 948.

(31) M. S. Kharasch, C Walling, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1559.

atoms, and thus the normal and the abnormal reactions may not always give products with reciprocal compositions. In the special case where the distribution of the bromine atoms is a reciprocal of that of the hydrogen atoms, the compositions of the products will be equal in spite of the quite different modes of reactions. Such examples will be found in case the nature of the substituents exerts a decisive influence on the determination of the positions which the bromine atoms and the hydrogen atoms can take irrespective of the order of addition.

Conclusion and Summary. When hydrogen bromide acts on the ethenoid linkage in the presence of oxygen, the first change to be characterized is the formation of a bromo radical from the unsaturated molecule and the bromine atom formed from hydrogen bromide and oxygen. In the formation of the bromo radical, if the double bond is situated at the end of a chain, the bromine atom takes preferably the terminal position, and, if an asymmetric carbon atom is produced by the addition of the bromine atom, inversion is accompanied. In the second stage of the reaction the radical, according as its nature and the conditions, either takes up hydrogen atom from hydrogen bromide to form a completed addition product and another bromine atom or splits off the bromine atom to regenerate the double bond. In either case the cycle of the changes is propagated by a chain mechanism. The action of oxygen, therefore, resembles that of light quantum in a photochemical reaction proceeding with a great quantum yield.

The theory advanced in this paper is based on the experiments on the action of hydrogen bromide and oxygen on certain ethenoid compounds.

The effect of reduced nickel will be discussed in a separate paper on the basis of a quite similar mechanism.

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