The Oxygen Effect in the Hydrogen Bromide Catalysis of the Addition Reaction of Bromine to Cinnamic Acid in Carbon Tetrachloride Solution.

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The addition reaction of bromine to ethenoid compounds is affected by a number of factors, e.g., the nature of walls of reaction vessels, exposure to light, and presence of oxygen, hydrogen bromide, etc.; therefore, a rigid control of experimental conditions is required to secure any significant results. The discovery by D. M. Williams and T. C. James(1), that hydrogen bromide, eliminating the induction period observed in addition reactions of bromine to certain ethenoid compounds, accelerates the reactions to a great extent, is of general importance, for at least some of the irregularities often observed in the bromine addition under apparently identical conditions could be attributed to the effect of hydrogen bromide present as an impurity or produced by accompanying substitution reaction in the course of the addition reactions. S. V. Anantakrishnan and R. Venkataraman(2) have tentatively suggested for the catalysis a mechanism involving the polarisation of the double bond and the activation of the bromine molecule by hydrogen bromide. This is far from satisfactory especially because the nature of the proposed activation is yet to be explained.

On the other hand, oxygen was found to inhibit the photochemical addition of chlorine to tetrachloroethylene in gas phase(3) and in carbon

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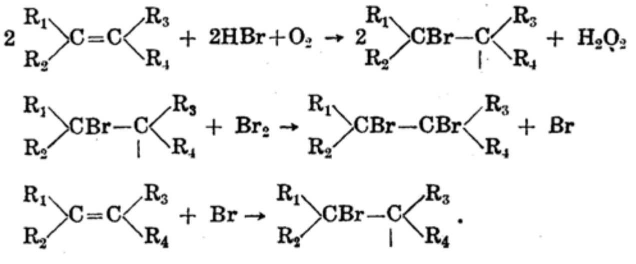
(1) D. M. Williams and T. C. James, *J. Chem. Soc.*, **1928**, 343.

(2) S. V. Anantakrishnan and R. Venkataraman, *ibid.*, **1939**, 224.

(3) R. G. Dickinson and J. L. Carrico, *J. Am. Chem. Soc.*, **56** (1934), 1473.

tetrachloride solution⁽⁴⁾; and subsequently W. H. Bauer and F. Daniels⁽⁵⁾ showed that also in the dark oxygen exerts an inhibitory effect on the bromine addition to cinnamic acid in carbon tetrachloride. Y. Urushibara and M. Takebayashi⁽⁶⁾ investigated the reaction with varying amounts of oxygen: the rate decreased sharply as the amount of oxygen increased. They also found an accelerating influence of benzoyl peroxide. The inhibitory effect of oxygen in the photochemical bromination is now explained⁽⁷⁾ as the result of capture by oxygen of free bromo radicals which would otherwise react with bromine to propagate the chains started by the action of light.

Earlier investigators in the field of the addition reactions of bromine paid no attention to the effect of oxygen and worked in the presence of air, although some of them excluded light deliberately to avoid the incursion of the photochemical process. In view of the inhibitory effect of oxygen the induction period is considered to be in all probability due to oxygen and it seemed that hydrogen bromide might not be in itself a catalyst for the addition of bromine, but its role might consist in the removal of oxygen inadvertently present in the reacting solution, thus restoring the reaction to its normal course. There was, however, an alternative: The researches⁽⁸⁾ in this laboratory on the oxygen effect in the addition of hydrogen bromide to ethenoid compounds have revealed that hydrogen bromide reacts with oxygen in the presence of ethenoid compounds, free bromo radicals being intermediately formed. If bromine is allowed to add in the presence of hydrogen bromide and oxygen, it will react with the bromo radical thus produced to yield the final product of the addition reaction and a bromine atom, which will attach itself to a molecule of the ethenoid compound regenerating another bromo radical, and this in turn will react with bromine to continue the chain reaction:



$$2\;{}^{R_1}_{R_2}\!\!>C=C<^{R_3}_{R_4} + 2HBr + O_2 \rightarrow 2\;{}^{R_1}_{R_2}\!\!>CBr-\underset{|}{C}<^{R_3}_{R_4} + H_2O_2$$

$${}^{R_1}_{R_2}\!\!>CBr-\underset{|}{C}<^{R_3}_{R_4} + Br_2 \rightarrow {}^{R_1}_{R_2}\!\!>CBr-CBr<^{R_3}_{R_4} + Br$$

$${}^{R_1}_{R_2}\!\!>C=C<^{R_3}_{R_4} + Br \rightarrow {}^{R_1}_{R_2}\!\!>CBr-\underset{|}{C}<^{R_3}_{R_4}.$$

The chains propagated by these radicals and atoms are essentially identical with those generally postulated for photochemical addition reactions. Thus, in this mechanism oxygen and hydrogen bromide will co-operate in causing a rapid addition reaction. The latter possibility has been proved

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(4) R. G. Dickinson and J. A. Leermakers, *J. Am. Chem. Soc.*, **54** (1932), 3852; J. A. Leermakers and R. G. Dickinson, *ibid.*, **54** (1932), 4648.

(5) W. H. Bauer and F. Daniels, *ibid.*, **56** (1934), 2014.

(6) Y. Urushibara and M. Takebayashi, this Bulletin, **12** (1937), 356, 499.

(7) R. F. Brown and F. Daniels, *J. Am. Chem. Soc.*, **62** (1940), 2820; W. Bockemüller and L. Pfeuffer, *Ann.*, **537** (1939), 178.

(8) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), 717; Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323; O. Simamura, *ibid.*, **15** (1940), 292.

to be the case in the bromine addition of cinnamic acid in carbon tetrachloride solution as will be discussed in the present paper on the basis of the experiments conducted with due consideration for the effects of oxygen and hydrogen bromide.

Materials. Commercial bromine of chemically pure grade was shaken with water,(9) refluxed with aqueous potassium bromide, and distilled. It was then dried by shaking with concentrated sulphuric acid and finally fractionated under reduced pressure. Cinnamic acid was purified by recrystallisation from hot water and then from aqueous alcohol.

Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and distilled through a Widmer column. The boiling range was less than 0.1°. Then it was shaken with phosphorus pentoxide and distilled, the middle fraction being collected.

Hydrogen bromide was generated by dropping bromine to hot tetralin, passed through a washing bottle containing cold tetralin and then through a tube filled with anthracene. The gas was dried with phosphorus pentoxide and collected in a tube cooled with liquid air. Then the condensed hydrogen bromide was subjected to repeated melting and solidification followed by evacuation to eliminate traces of incondensable gases and finally to fractionation, the middle portion being used.

Hydrogen chloride was generated by dropping concentrated hydrochloric acid to concentrated sulphuric acid, bubbled through concentrated sulphuric acid, collected in a bulb cooled with liquid air, and purified in the same way as hydrogen bromide.

Experimental Procedure. The general procedure was as follows: In a glass tube with a capacity of 57 c.c. a small sealed bulb containing an accurately weighed amount of bromine (0.13–0.15 g.) was placed and a measured quantity of a carbon tetrachloride solution (about 20 c.c.) of cinnamic acid (the concentration, 0.034 mol./l.) was introduced from a burette so that, when the bulb with bromine was broken, a solution containing 0.045 mole of bromine per litre might result. The level of the meniscus of the solution was marked on the tube by labelling a strip of paper and 5 c.c. of carbon tetrachloride was added. The tube was connected to the vacuum line and evacuated. Carbon tetrachloride was distilled off until the meniscus reached the mark, the tube was then cooled with liquid air and further evacuated with a mercury diffusion pump. Such a procedure of removing oxygen dissolved in the carbon tetrachloride solution was adopted in preference to repeated solidification of the solution by cooling with liquid air, followed by evacuation and melting, because the former was far more rapid, although it involved a slight but unimportant sacrifice of accuracy in the concentration of the solution. Then a measured volume of hydrogen bromide gas was condensed on the top of the solidified mixture, oxygen was introduced to a specified pressure, and the tube was sealed off and taken out of the liquid air bath. It was protected from light throughout the procedure after the admission of hydrogen bromide. When the contents of the tube melted, which took usually 45 minutes, the reaction was started by breaking the bulb containing bromine by shaking the sealed tube. The tube was left in the dark at room temperature (10 to 12°) for eleven hours and twenty minutes. Then its tip was broken in a two percent aqueous solution of patassium iodide and the liberated iodine was titrated with decinormal thiosulphate.

The Uncatalyzed Addition and the Effect of Oxygen. Typical examples of the results are summarized in the accompanying table. Extent of addition in the last column denotes the percentage of the cinnamic acid which reacted with bromine in eleven hours and twenty minutes as calculated from the decrease in the amount of bromine. The reaction in the absence of added substances was not reproducible, the extent of addi-

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(9) P.C.E.M. Terwogt, *Z. anorg. Chem.*, **47** (1905), 203.

tion ranging from 45 to 55% (Exp. 22 and 35). It is not certain whether this was caused by small traces of oxygen which may have been still present in the reaction mixture or by any other disturbing factors which escaped experimental control. Nevertheless, it is clear that the reaction occurred much faster in the absence of oxygen than in the presence, as 0.13 millimole of oxygen admitted (of which 0.018 millimole is dissolved in the solution(10)) diminished the extent of addition to 8% (Exp. 11). These values are considered to be reasonable in comparison with those obtained by Y. Urushibara and M. Takebayashi(6), if differences in the experimental conditions, especially in temperature and reaction time, are taken into account.

Table. The Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride Solution in the Dark. Reaction temperature, 10–12°C; reaction time, 11 hours 20 minutes; bromine (0.13–0.15 g.), 0.045 mol./l.; cinnamic acid, 0.034 mol./l.

Exp. No.	Added Substances (millimole)	Extent of Addition (%)
22	None	45.3
35	None	55.1
2*	O_2, 0.11	11.1
11	O_2, 0.13	8.1
17	HBr, 0.92	32.8
18	HBr, 0.92	35.4
40	HBr, 0.92	36.4
25	HBr, 0.18	25.0
39	HBr, 0.18	22.2
19	HBr, 0.92; O_2, 0.02	89.7
20	HBr, 0.92; O_2, 0.05	99.2
26	HBr, 0.20; O_2, 0.02	98.0
27	HBr, 0.20; O_2, 0.09	96.8
28	HBr, 0.20; O_2, 0.21	94.5
31	HCl, 0.18	27.4
32	HCl, 0.92	14.6
33	HCl, 0.18; O_2, 0.11	2.6
34	HCl, 0.92; O_2, 0.11	3.6
36	Catechol, 5 mg.	27.3†
42	Catechol, 5 mg.; HBr, 0.18; O_2, 0.02	30.5†
23	Tetrabromohydroquinone, 20 mg.	5.5
29	Tetrabromohydroquinone, 25 mg.; HBr, 0.37; O_2, 0.11	94.1
37	H_2O, 2.3 mg.	41.0
38	H_2O, 2.3 mg.; HBr, 0.18	47.5

* The reaction time 17 hours 40 minutes.

† Apparent extent of addition.

Effect of Hydrogen Bromide. Contrary to the expectation from existing experimental data it was found that in the presence of hydrogen bromide the reaction never proceeded faster than in the absence. It appears rather to exert a retarding effect. Complication arises, however, because the retardation did not increase with the amount of hydrogen bromide admitted, the extent of addition being distinctly less with a smaller amount of hydrogen bromide (Exp. 25 and 39) than with a larger amount (Exp. 17, 18, and 40). The observed facts may be due to the contamination of hydrogen bromide or other reagents with traces of oxygen, the simultaneous presence of hydrogen bromide and oxygen accelerating the addition reaction as will be discussed below. Oxygen, however, must have been present in a very small amount, because the

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(10) Calculated from the distribution coefficient of oxygen given by J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17** (1931), 213.

retardation due to hydrogen bromide was overcome only partly in spite of the strong accelerating effect of oxygen and hydrogen bromide; it seems that the retardation by hydrogen bromide increases not so sharply with the amount of hydrogen bromide as the counteracting acceleration by oxygen and hydrogen bromide does. The hypothesis suggested by S. V. Anantakrishnan and R. Venkataraman(2) that hydrogen bromide activates the reactants is no longer tenable.

Combined Action of Hydrogen Bromide and Oxygen. Experiments were carried out with 0.20 to 0.92 millimole of hydrogen bromide and 0.02 to 0.21 millimole of oxygen. The extents of addition were greater than 90% under these experimental conditions, showing that the reaction proceeds faster in the presence of both hydrogen bromide and oxygen together than in the absence of either or even both of them. This demonstrates convincingly the anticipated co-operation of hydrogen bromide and oxygen in causing a rapid addition reaction; and the possibility already referred to, that hydrogen bromide might be effective by merely eliminating the inhibiting oxygen, is excluded. On the basis of the data obtained, however, nothing can be said with regard to how the extent of addition is influenced by variation in amounts of the admitted gases.

Influence of Hydrogen Chloride. In contrast with the experiments with hydrogen bromide and oxygen, when hydrogen chloride was substituted for hydrogen bromide, no acceleration was observed at all, the pronounced inhibition being due to oxygen. If traces of oxygen which might still be present in the hydrogen chloride purified by fractionation in vacuum were not sufficient to reduce the rate of addition markedly, the fact that the extent of addition in Exp. 32 was found lower than Exp. 31 may be considered to indicate a retardation by hydrogen chloride. Its failure to co-operate with oxygen shows that the role of hydrogen bromide is as unique here in the bromine addition as in the addition of hydrogen bromide to ethenoid compounds in the presence of oxygen(11) and in the cis-trans isomerisation(12) caused by the joint action of hydrogen bromide and oxygen; consequently a natural inference is that a common mechanism is in operation in all these reactions.

Effect of Antioxidants. A further evidence to support this view is afforded by the experiments in which the effects of antioxidants were examined. When 5 mg. (4.6×10^{-5} mole) of catechol was added to the reaction mixture, the extent of addition was diminished to about 30% whether both hydrogen bromide and oxygen were present or not. The extent of addition was only apparent in this case, because catechol consumed bromine. A separate experiment showed that one mole of catechol reacted with two moles of bromine in three hours and with a little more in seven hours, the concentrations of the reactants being the same as those obtaining in the addition reaction, whereas Zincke(13) stated that he

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(11) A series of papers by Y. Urushibara and M. Takebayashi beginning with this Bulletin, **11** (1936), 692. Cf. reference 8.

(12) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507; **13** (1938), 566. O. Simamura, *ibid.*, **14** (1939), 294.

(13) Th. Zincke, *Ber.*, **20** (1887), 1777.

obtained tetrabromocatechol by the action of bromine on catechol in chloroform. On the assumption that one mole of catechol reacted with two moles of bromine, the extent of addition for Exp. 36 and 42 are to be corrected to 13.6 and 18.5%, respectively. If the action of bromine on catechol in the reaction mixture yielded tetrabromocatechol, the corrected values should be zero and 3.1%, respectively. In any case the effectiveness of catechol in repressing the joint action of hydrogen bromide and oxygen has been demonstrated beyond doubt. Catechol represses the oxygen effect also in the addition of hydrogen bromide and in the cis-trans isomerisation. The similarity in this respect substantiates the view that a common mechanism is operating.

Tetrabromohydroquinone, with no nuclear hydrogen to react with bromine, was examined. Twenty mg. of it added to the reacting solution, though the greater part remained undissolved, was found to retard the uncatalyzed reaction of bromine, but it could not repress the rapid reaction caused by hydrogen bromide and oxygen. Its ineffectiveness may be attributed to its low solubility in carbon tetrachloride.

A significance to be attached to the retardation of the uncatalyzed reaction by catechol and tetrabromohydroquinone will be discussed below.

Effect of Water. In the reaction of hydrogen bromide and oxygen in the presence of the ethenoid compound water is one of the final products(8); therefore, the effect of traces of water had to be investigated to ascertain that it would not be an important agent in the catalysis by hydrogen bromide and oxygen. Water was introduced into the reaction tube, which had been evacuated and cooled with liquid air as described above, by heating sodium sulphate decahydrate, contained in an amount to yield 1.3×10^{-4} mole of water in a tube connected to the vacuum line. This amount of water nearly saturated the carbon tetrachloride solution.(14) Now, water was found to exert no conspicuous effect on the addition of bromine in the absence of any other added substances, but it compensated partly the slight retardation by hydrogen bromide. Inasmuch as the amount of water introduced here is much greater than what would have been produced by the complete conversion of the oxygen admitted (0.02 millimole) in Exp. 26, for which the extent of addition was 98.0%, it is concluded that the enormous effect caused by the joint action of oxygen and hydrogen bromide cannot be attributed to the action of water to be ultimately formed from them.

Conclusion. On the basis of the observations fully discussed above the nature of the hydrogen bromide catalysis in the addition of bromine to cinnamic acid has been elucidated. Thus, in order that hydrogen bromide can exert a catalytic action, the co-operation of oxygen is necessary. They start the chain reaction involving bromine atoms and free radicals just as exposure of the reaction mixture to light does. A generalisation of the proposed mechanism will no doubt be feasible in view of numerous instances of "the hydrogen bromide catalysis in the addition reaction of bromine" recorded in the literature.

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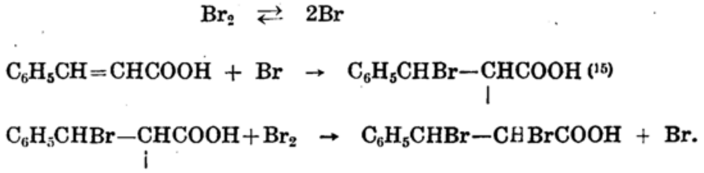
(14) Cf. Rosenbaum and Walton, *J. Am. Chem. Soc.*, **52** (1930), 3571.

The effectiveness of antioxidants, such as catechol and tetrabromohydroquinone, in preventing the uncatalysed addition of bromine in the dark in carbon tetrachloride solution as well as that of oxygen is understandable if it is assumed that the chain mechanism as shown in the following scheme is predominantly in operation also in the dark and that they inhibit the reaction by functioning as chain breakers.



$$Br_2 \rightleftarrows 2Br$$

$$C_6H_5CH{=}CHCOOH + Br \rightarrow C_6H_5CHBr{-}\underset{|}{C}HCOOH^{(15)}$$

$$C_6H_5CHBr{-}\underset{|}{C}HCOOH + Br_2 \rightarrow C_6H_5CHBr{-}CHBrCOOH + Br.$$

The view is favoured by the theoretical consideration by A. Sherman, O. T. Quimby, and R. O. Sutherland(17), who, on the basis of the semi-empirical calculation of activation energies, were led to expect that the addition of bromine to an ethenoid double bond might follow the course involving bromine atoms and free radicals rather than that involving the bimolecular combination of bromine with a double bond. The calculation applies only to the reaction in gas phase, but it is not unreasonable to assume that carbon tetrachloride as a solvent would cause no appreciable change in the activation energies of the reaction.

Summary.

It has been found that a joint action of hydrogen bromide and oxygen accelerates the addition of bromine to cinnamic acid in carbon tetrachloride solution in the dark, whereas the reaction is retarded by either of them. The catalyzed reaction is prevented by catechol, and hydrogen chloride cannot be substituted for hydrogen bromide without the disappearance of the accelerating effect. On the basis of these observations the nature of the alleged catalysis of the addition of bromine by hydrogen bromide has been elucidated. The elimination of the induction period, which is certainly attributable to the inhibitory action of oxygen, is not due to the removal of the latter. The explanation offered is that hydrogen bromide and an ethenoid compound in co-operation with the very oxygen starts a rapid chain reaction involving bromine atoms and free radicals. Also for the uncatalyzed addition of bromine to cinnamic acid in carbon

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(15) In this scheme the bromine atom is assumed to attach itself to the β carbon atom of cinnamic acid, because crotonic acid has been found to add hydrogen bromide to yield β-bromobutyric acid even in the presence of oxygen, i.e., under the conditions where the mechanism involving bromine atoms is operative,(16) and cinnamic acid is known to give always β-bromohydrocinnamic acid.(17)

(16) O. Simamura, shortly published in this Bulletin.

(17) A. Michael, *J. Org. Chem.*, **4** (1939), 123.

(18) A. Sherman, O. T. Quimby and R. O. Sutherland, *J. Chem. Phys.*, **4** (1936), 732.

tetrachloride a possibility of a mechanism involving chains has been suggested.

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