# The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds and the Influence of Catechol.

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The addition of hydrogen bromide to allyl bromide and to undecenoic acid follows the Markownikoff rule in the absence of peroxides and oxygen to yield the normal products, 1,2-dibromopropane and 10-bromoundecanoic acid respectively, while in the presence of peroxides or oxygen the direction of addition is reversed, the abnormal products, 1,3-dibromopropane and 11-bromoundecanoic acid respectively, being formed; and the presence of an antioxidant, e.g. catechol, hydroquinone, diphenylamine, etc., in the reacting mixture gives rise to the formation of the normal products even in the presence of peroxides or oxygen.(1) The peculiar effect of oxygen in co-operation with hydrogen bromide has been found also in the isomerization of isostilbene(2) and methyl allo-cinnamate(3) to their respective geometrical isomerides, catechol being likewise effective in inhibiting the reaction.(2)

A contribution to the explanation of the oxygen effect was made by Y. Urushibara and O. Simamura(4) when they passed hydrogen bromide and oxygen into allyl bromide in the dark at 0°C. and observed the complicated reactions to take place. As the result of the reactions free bromine, water, 1,2,3-tribromopropane, and an organic peroxide, were formed along with 1,3-dibromopropane, the main product. Thus it was indicated that bromine is liberated from hydrogen bromide and oxygen in the presence of the ethenoid compound and the reactions involved were represented as follows:

$$2\,\mathrm{CH_2{=}CH{-}CH_2Br} + 2\,\mathrm{HBr} + \mathrm{O_2} \rightarrow 2\,\mathrm{BrCH_2{-}\underset{|}{C}H{-}CH_2Br} + \mathrm{H_2O_2} \quad (1),$$

$$\mathrm{BrCH_2{-}\underset{|}{C}H{-}CH_2Br} + \mathrm{HBr} \rightarrow \mathrm{BrCH_2{-}CH_2{-}CH_2Br} + \mathrm{Br} \quad (2),$$

$$\mathrm{CH_2{=}CH{-}CH_2Br} + \mathrm{Br} \rightarrow \mathrm{BrCH_2{-}\underset{|}{C}H{-}CH_2Br} \quad (3),$$

$$2\,\mathrm{BrCH_2{-}\underset{|}{C}H{-}CH_2Br} + \mathrm{O_2} \rightarrow \mathrm{(BrCH_2)_2CH{-}O{-}O{-}CH(CH_2Br)_2} \quad (4),$$

$$\mathrm{H_2O_2} + 2\,\mathrm{HBr} \rightarrow 2\,\mathrm{H_2O} + \mathrm{Br_2} \quad (5),$$

$$\mathrm{CH_2{=}CH{-}CH_2Br} + \mathrm{Br_2} \rightarrow \mathrm{BrCH_2{-}CHBr{-}CH_2Br} \quad (6).$$

The starting reaction is the oxidation of hydrogen bromide by oxygen with allyl bromide as a necessary acceptor of bromine atoms to yield hydrogen peroxide and a dibromoisopropyl radical. The radical thus

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(1) Compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461; *Ann. Rep.*, **1939**, 219.

(2) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507; **13** (1938), 566.

(3) O. Simamura, *ibid.*, **14** (1939), 294.

(4) Y. Urushibara and O. Simamura, *ibid.*, **14** (1939), 323.

formed reacts with hydrogen bromide to produce 1,3-dibromopropane and a bromine atom, and the latter combines with allyl bromide to give another dibromoisopropyl radical, thus the abnormal addition of hydrogen bromide to allyl bromide proceeding by a chain process. The organic peroxide may be such that is to be formed by the action of oxygen on the dibromoisopropyl radical. The hydrogen peroxide and hydrogen bromide produce free bromine and water, and the bromine combines with allyl bromide to yield 1,2,3-tribromopropane.

If oxygen is present only in a limited amount, reaction (1), consequently also reactions (4), (5), and (6), occur only to a small extent and thus the formation of the peroxide, water, bromine, and tribromopropane, may be imperceptible, while the abnormal addition giving 1,3-dibromopropane can proceed by the propagation of the chain reaction, (2) and (3). The inhibiting action of the antioxidants on the abnormal addition was formerly considered to consist in capturing the bromine atom and thus interrupting the propagation of the chain reaction. In the cis-trans-isomerization caused by hydrogen bromide and oxygen a bromo-radical is likewise formed intermediately from the unsaturated molecule and a bromine atom delivered by hydrogen bromide and oxygen, and the change proceeds by a chain reaction carried by the bromine atom. The inhibition of this isomerization by an antioxidant was also attributed to the break of the chain reaction due to the capture of the bromine atom.

The present paper records the results of experiments on the action of the mixture of hydrogen bromide and oxygen on various ethenoid compounds, some being incapable of adding bromine at all and others adding bromine only to a limited extent. The influence of catechol on the reactions has been examined with the result that the hypothesis on the inhibiting action of the antioxidant on the oxygen effect has been corrected.

**Materials.** Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a bottle containing cold tetralin and a tube filled with anthracene, and dried with phosphorus pentoxide. Oxygen was taken from a bomb and dried with phosphorus pentoxide.

Tetraphenylethylene was prepared from benzophenone according essentially to the direction of J. Lévy and R. Lagrave.(5) 1,1,1,2-Tetraphenylethanol-(2) (7 g.) was heated with acetyl chloride (30 c.c.) in a sealed tube at about 160° for four hours and tetraphenylethylene produced was recrystallized from benzene, m.p. 225–226°; yield 4.5 g.

Dimethylmaleic anhydride was prepared according to E. Ott.(6) Dimethyl dimethylfumarate and dimethyl dimethylmaleate were synthesized by refluxing dimethylfumaric acid and dimethylmaleic anhydride respectively with methanol containing 10% of concentrated sulphuric acid. The dimethylfumarate melted at 42–44° after recrystallization from petroleum ether and the dimethylmaleate boiled at 98° under a pressure of 6 mm., $n_D^{20}$ 1.4570. Dimethylfumaric acid was obtained by boiling dimethylmaleic anhydride with concentrated aqueous sodium hydroxide according to Fittig,(7) m.p. 250–251°.

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(5) J. Lévy and R. Lagrave, *Bull. soc. chim.*, [4], **43** (1928), 440.

(6) E. Ott, *Ber.*, **61** (1928), 2131.

(7) R. Fittig, *Ann.*, **304** (1899), 158.

Tetraethyl α,γ-dicarboxy-α-bromoglutaconate and tetraethyl α,γ-dicarboxy-α-methylglutaconate were prepared by the action of bromine⁽⁸⁾ and methyl iodide⁽⁹⁾ respectively on tetraethyl α,γ-dicarboxy-α-sodioglutaconate obtained from diethyl malonate, chloroform and sodium ethoxide.

1,1-Diphenylethylene was prepared by the method described in the "Organic Syntheses." Allyl bromide was purified by washing with dilute aqueous sodium carbonate and then with water, drying with anhydrous calcium chloride, and distilling in dim light. The product thus purified was free from peroxide (no colouration with ferrous ammonium sulphate and ammonium thiocyanate). Catechol was a product of Merck and phenanthrene of Schering-Kahlbaum.

**The Action of the Mixture of Hydrogen Bromide and Oxygen on the Ethenoid Compounds.** Tetraphenylethylene does not add bromine,(10) and it has also been shown that the action of hydrogen bromide on tetraphenylethylene glycol results in the formation of tetraphenylethylene and free bromine instead of tetraphenylethylene dibromide.(11) Into a solution of tetraphenylethylene (0.2 g.) in benzene (50 c.c.) the mixture of hydrogen bromide and oxygen was passed for one hour in the dark at room temperature. No liberation of bromine was noticed. On removal of benzene in vacuum at room temperature the starting material was recovered. The elevation of the temperature to 40–50° did not cause any reaction.

With dimethylmaleic anhydride (0.6 g. in 30 c.c. of benzene) which adds no bromine,(12) no reaction took place under similar conditions.

In phenanthrene the bond between carbon atoms 9 and 10 has a pronounced double bond character as is shown, for example, by the formation of a dibromide.(13) When phenanthrene (0.8 g. in 30 c.c. of benzene or 0.1 g. in 30 c.c. of carbon tetrachloride) was treated with hydrogen bromide and oxygen for one hour, no liberation of bromine occurred and from the solutions thus treated the original material was recovered.

When the gas mixture was passed into a carbon tetrachloride solution of tetraethyl α,γ-dicarboxy-α-bromoglutaconate (0.35 g.–0.6 g. in 30 c.c.), which adds bromine to a small extent,(14) an immediate and copious formation of bromine was observed. The amount of bromine liberated, however, did not seem to increase indefinitely even when the passage of the gas mixture was continued.

With tetraethyl α,γ-dicarboxy-α-methylglutaconate (0.64 g. in 30 c.c. carbon tetrachloride), which adds bromine to some extent,(15) only a small

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(8) M. Guthzeit and E. Hartmann, *J. prakt. Chem.*. **81** (1910), 329.

(9) F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99** (1911), 2196.

(10) H. Biltz, *Ann.*, **296** (1897), 219; H. Finkelstein, *Ber.*, **43** (1910), 1533.

(11) W. Madelung and M. Oberwegner, *Ber.*, **60** (1927), 2469.

(12) A. Michael, *J. prakt. Chem.*, **46** (1892), 382.

(13) L. F. Fieser and C. C. Price, *J. Am. Chem. Soc.*, **58** (1936), 1834.

(14) Private communication from Y. Urushibara: When bromine and the bromo-ester are mixed, the change in the colour intensity and the evolution of heat are hardly noticed, but on removing the free bromine by washing the mixture in ethereal solution with aqueous sodium sulphite and evaporating the ethereal solution, bromine is split off, showing that an addition product has been formed and exists in equilibrium with the unsaturated bromo-ester and free bromine. Thus the behaviour of the bromo-ester towards bromine is qualitatively the same as that of tetraethyl α,γ-dicarboxy-α-methylglutaconate(15) but the bromine addition takes place to a smaller extent.

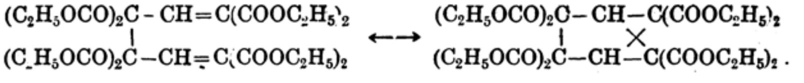
(15) Y. Urushibara, this Bulletin, **3** (1928), 200.

amount of bromine was liberated, and after removal of carbon tetrachloride there remained an unstable oily product having a content of bromine corresponding to the addition of one molecule of hydrogen bromide.

1,1-Diphenylethylene (0.1 g.) in carbon tetrachloride (30 c.c.) liberated bromine on treatment with hydrogen bromide and oxygen.

Dimethyl dimethylfumarate was found to add neither bromine nor hydrogen bromide in carbon tetrachloride in the dark, but on treatment of the ester with hydrogen bromide and oxygen bromine was liberated: A carbon tetrachloride solution containing 0.0010 mole of bromine and 0.0009 mole of the ester in 100 c.c. and a control solution containing only bromine were prepared in the dark and the intensities of the colour of the two solutions were compared with a Pulfrich photometer; after 116 days' standing in the dark any difference were still imperceptible. Into a carbon tetrachloride solution of the dimethylfumarate (0.4 g. in 30 c.c.) hydrogen bromide was passed for one hour; and the ester was recovered unchanged on evaporation of the solvent. On passing hydrogen bromide and oxygen under similar conditions the formation of bromine was rapid and proceeded similarly as with tetraethyl $\alpha,\gamma$-dicarboxy-$\alpha$-bromoglutaconate. On removal of carbon tetrachloride in vacuum, a viscous oil remained, which liberated bromine gradually. (For quantitative experiment see below.) Dimethyl dimethylmaleate behaved towards the mixture of hydrogen bromide and oxygen in a similar manner.

A further instance of bromine liberation in the presence of an ethenoid compound which adds no bromine is afforded by a compound, $C_{30}H_{42}O_{16}$, m.p. 86°, obtained by the action of iodine on tetraethyl $\alpha,\gamma$-dicarboxy-$\alpha$-sodio-glutaconate.(8)(16) M. Guthzeit and E. Hartmann(8) ascribed to this substance a bicyclobutane structure, which was deduced on the basis of a series of peculiar changes it showed. It is remarkable that it exhibited no indication of unsaturation. More recently C. K. Ingold and coworkers(17) examined the substance and also the corresponding methyl ester and they confirmed the saturated character of the compound except that they obtained oxalic acid and tetraethyl ethanetetracarboxylate by ozonolysis. They explained the remarkable behaviours by assuming a mesomerism between the following structures:



$$\begin{array}{l}(C_2H_5OCO)_2C-CH=C(COOC_2H_5)_2\\ \qquad\qquad\quad |\\ (C_2H_5OCO)_2C-CH=C(COOC_2H_5)_2\end{array} \longleftrightarrow \begin{array}{l}(C_2H_5OCO)_2C-CH-C(COOC_2H_5)_2\\ \qquad\qquad\quad |\qquad\ \times\\ (C_2H_5OCO)_2C-CH-C(COOC_2H_5)_2\,.\end{array}$$

Now, the introduction of hydrogen bromide and oxygen into a carbon tetrachloride solution of the compound in question (0.58 g. in 30 c.c.) caused an immediate liberation of bromine, thus revealing the unsaturation of the compound.

The experimental results described above, although they give no simple rule for the relation between the bromine addition of an ethenoid compound and the liberation of bromine on treating it with hydrogen

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(16) Private communication from Y. Urushibara: The same dimeric derivative is formed along with tetraethyl $\alpha,\gamma$-dicarboxy-$\alpha$-sodio-glutaconate, free iodine, and sodium bromide on heating tetraethyl $\alpha,\gamma$-dicarboxy-$\alpha$-bromoglutaconate with sodium iodide in alcoholic solution.

(17) C. K. Ingold, M. M. Parekh, and C. W. Shoppee, *J. Chem. Soc.*, **1936**, 142.

bromide and oxygen, can be well understood from the reaction mechanism as developed for the case of allyl bromide. The bromine liberation must be preceded by the starting reaction, which depends on the nature of the ethenoid compound. If the ethenoid compound is unable to take up a bromine atom to form a bromo-radical, then no reaction takes place at all. If the ethenoid compound is able to act as an acceptor of the bromine atom, then a bromo-radical and hydrogen peroxide are formed as in the case of allyl bromide:

$$2\,\mathrm{RR'C{=}CR''R'''} + 2\,\mathrm{HBr} + \mathrm{O_2} \rightarrow 2\,\mathrm{RR'BrC{-}}\underset{|}{\mathrm{C}}\mathrm{R''R'''}\ (\text{or } \mathrm{RR'}\underset{|}{\mathrm{C}}\mathrm{{-}CBrR''R'''}) + \mathrm{H_2O_2}.$$

The hydrogen peroxide produces free bromine by acting on hydrogen bromide. The free bromine appears at once if the ethenoid compound does not add the bromine or the bromine addition product is easily dissociable. If the ethenoid compound gives a stable bromine addition product, then free bromine remains as such only after, or just when, all the unsaturated compound has disappeared, but, as hydrogen peroxide can not be produced without the unsaturated compound, the bromine liberation can never be carried on beyond a certain limit. The bromo-radical may form a peroxide with oxygen on one hand, and, on the other, may either start the chain reaction of an abnormal addition of hydrogen bromide, or take up another bromine atom to form a dibromide, or split off the bromine atom to regenerate the double bond, according to its nature. In any case the liberation of bromine on treatment with hydrogen bromide and oxygen may be regarded as a possible, if not always occurring, symptom of the ethenoid double bond.

**The Influence of Catechol on the Reactions.** When the mixture of hydrogen bromide and oxygen was passed for one hour into a solution of dimethyl dimethylfumarate (0.33 g., 0.002 mole) in carbon tetrachloride (30 c.c.) with the addition of a small amount (15 mg., 7 moles per cent to the ester) of catechol and the solvent was removed in vacuum at room temperature, there remained a mass of crystals. This was extracted with water and then with ether. On evaporating the two extracts catechol and dimethyl dimethylfumarate were recovered. Thus catechol inhibited completely the liberation of bromine from hydrogen bromide and oxygen in the presence of dimethyl dimethylfumarate. On the other hand, on passing the gas mixture into a carbon tetrachloride solution of 0.0024 mole of the ester in absence of catechol about 0.0014 gram atom of bromine was set free besides 0.0026 gram atom combined in the oily product. The enormous capacity of catechol to inhibit the reaction was further demonstrated by an experiment with allyl bromide:

The remarkable reactions of allyl bromide with the mixture of hydrogen bromide and oxygen have been described briefly above or in details in the previous paper.(4) The addition of a small amount of catechol caused a complete inhibition of the reactions: The gas mixture was passed into 20.2 g. (0.17 mole) of allyl bromide containing 20 mg. (0.00018 mole, about 0.001 mole to 1 mole of allyl bromide) for six hours in the dark at 0°, and the reaction mixture was washed several times with water, dried with calcium chloride, and distilled. The whole passed over at the boiling point of allyl bromide (70°). Thus it has been shown that, although an unlimited amount of oxygen is available, a very small amount of catechol is capable of inhibiting totally all the reactions observed in the absence of catechol. It seems that the normal addition, being slow compared with the abnormal, was unnoticeable in six hours at 0°.

In the previous experiments without catechol, one mole of allyl bromide gave the organic peroxide in an amount corresponding to 0.1 to 0.2 gram atom of iodine. The mechanism represented above requires the formation of at least 0.1 to 0.2 gram atom of bromine, to which the amount of tribromopropane obtained in practice nearly corresponded. Nevertheless, it is very evident that 0.001 mole of catechol can never match 0.1 to 0.2 gram atom of bromine in any chemical process whatever.

Further it was ascertained that catechol can not inhibit the reaction of hydrogen bromide and hydrogen peroxide (in aqueous solution).

All the facts point that the very starting reaction (1) is inhibited in the presence of catechol, thus suggesting some analogy with the inhibiting action of antioxidants on the autoxidation of aldehydes.

As for the mechanism of the inhibition by the antioxidants, what has been said of the experiments with an unlimited excess of oxygen applies at once to those with a limited amount of oxygen. Thus it is clear that the antioxidants inhibit the oxygen effect, not by capturing bromine atoms carrying the chain reaction of the abnormal addition or the isomerization, but by stopping the starting reaction giving a bromo-radical and hydrogen peroxide from an ethenoid compound, hydrogen bromide and oxygen.

The inhibiting actions of antioxidants on the effect of reduced nickel and on the light effect must be quite different matters. Reduced nickel produces an effect similar to that of oxygen not only in the addition reaction(18) but also in the isomerization,(2) and catechol prevents the effect. In this case the cause of the inhibition may be found in the adsorption of catechol on reduced nickel or in the capture of bromine atoms by catechol.(19) Isostilbene is isomerized to stilbene by hydrogen bromide in sunlight in absence of oxygen, and catechol inhibits this isomerization in sunlight.(20) In this case it must be assumed that the bromine atoms, produced from hydrogen bromide by the action of light and responsible for the isomerization, are consumed by the catechol, and no alternative explanation seems possible. An experiment on the relation between the amounts of hydrogen bromide and of catechol will throw light on this problem.

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(18) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51; **13** (1938), 331, 400, 404, 574; M. Takebayashi, *ibid.*, **15** (1940), 113, 116.

(19) Y. Urushibara, *J. Chem. Soc. Japan,* **60** (1939), 717.

(20) Y. Urushibara and O. Simamura, this Bulletin, **13** (1938), 566.