The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds. I

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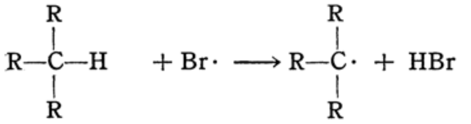
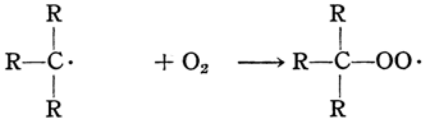
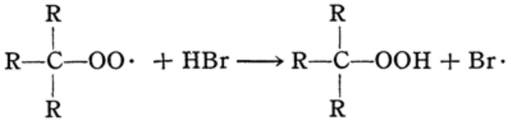
The mechanism of the hydrocarbon oxidation by means of molecular oxygen at room or higher temperature is very complicated and its study has been an object of many investigations for many years. Although the mechanism has not yet been completely elucidated, the recent progress of the free radical chemistry has made clear that the oxidation by molecular oxygen involves free radical intermediates in the course of the reaction. The research of the oxidation at room temperature is very interesting and important, but the relatively slow velocity of the reaction at room temperature makes difficult such an investigation. It has been found that many materials such as catechol and hydroquinone which can serve as hydrogen donors retard the oxidation. However, hydrogen bromide which is also one of the hydrogen donors is known to be a distinguished accelerator of the oxidation of hydrocarbons by molecular oxygen, as described by F.F. Rust and W.E. Vaughan[1]. They carried out an extensive investigation of the oxidation of aliphatic and aromatic hydrocarbons catalysed by hydrogen bromide, and they proposed the following mechanism for the reaction,



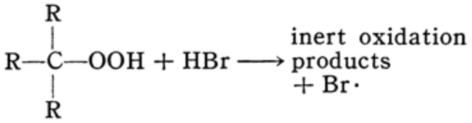
$$\mathrm{R{-}\overset{R}{\underset{R}{C}}{-}H} + \mathrm{Br}\cdot \longrightarrow \mathrm{R{-}\overset{R}{\underset{R}{C}}}\cdot + \mathrm{HBr} \qquad 1)$$



$$\mathrm{R{-}\overset{R}{\underset{R}{C}}}\cdot + \mathrm{O_2} \longrightarrow \mathrm{R{-}\overset{R}{\underset{R}{C}}{-}OO}\cdot \qquad 2)$$

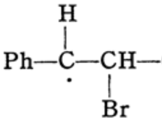


$$\mathrm{R{-}\overset{R}{\underset{R}{C}}{-}OO}\cdot + \mathrm{HBr} \longrightarrow \mathrm{R{-}\overset{R}{\underset{R}{C}}{-}OOH} + \mathrm{Br}\cdot \qquad 3)$$



$$\mathrm{R{-}\overset{R}{\underset{R}{C}}{-}OOH} + \mathrm{HBr} \longrightarrow \text{inert oxidation products} + \mathrm{Br}\cdot \qquad 4)$$

Y. Urushibara and O. Simamura[2] extended their study of oxygen effect in the addition of hydrogen bromide to ethenoid compounds to the action of the mixture of oxygen and hydrogen bromide on allyl bromide, crotonic acid, and several other compounds. O. Simamura and the present author[3] studied the joint action of hydrogen bromide and oxygen on cinnamic acid and determined the orientation of the bromine atom when it adds to the double bond of cinnamic acid. Namely, the free radical



$$\mathrm{Ph{-}\overset{H}{\underset{\cdot}{C}}{-}\underset{Br}{CH}{-}COOH}$$

is more likely formed as the intermediate rather than

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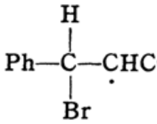
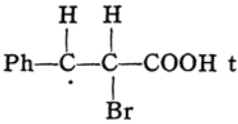
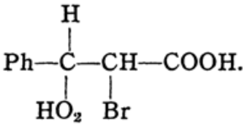
[1] F.F. Rust and W.E. Vaughan, *Ind. Eng. Chem.*, **41**, 2595 (1949).

[2] Y. Urushibara and O. Simamura, This Bulletin, **14**, 323 (1939).

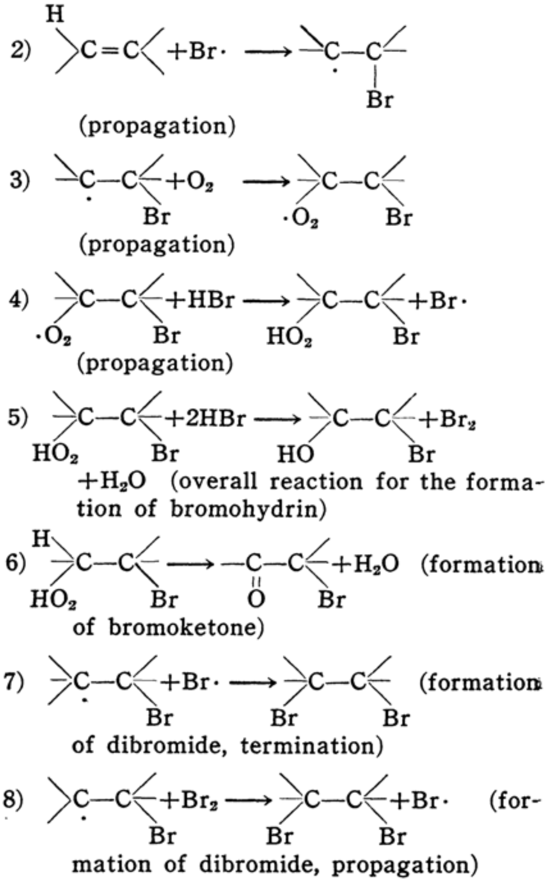
[3] O. Simamura and M. Takahasi, ibid., **22**, 60 (1949).

the alternative  $Ph-\overset{H}{\underset{Br}{C}}-\dot{C}HCOOH$, because ω-bromoacetophenone and carbon dioxide are obtained as the oxidation products and it can be supposed that they are derived from  $Ph-\underset{\cdot}{\overset{H}{C}}-\overset{H}{\underset{Br}{C}}-COOH$ through the hydroperoxide  $Ph-\overset{H}{\underset{HO_2}{C}}-\underset{Br}{CH}-COOH$. In order to compare the relative stability of these radicals theoretically, the author carried out a computation of the delocalization energies of the odd electron of the free radicals, $Ph-\dot{C}H_2$ and $\dot{C}H_2-COOH$, according to the same method as that which was adopted by G. W. Wheland[4], and obtained 15.3 kcal./mol. for the former and 16.7 kcal./mol. for the latter, assuming $S=0.25$, $\delta=0.8$, $\delta'=0$ and $\eta=0.8$. It may be impossible to conclude from these values that the latter is more stable than the former, for the calculation is of the zeroth order approximation. The values of bond dissociation energies of benzyl bromide and bromoacetic acid measured by the pyrolytic method of M. Szwarc[5] or that of toluene by the substitution reaction of bromine according to E. R. VanArtsdalen[6] will supply useful knowledge concerning this problem.

In this series of our papers the general scheme of the oxidation of various olefinic compounds in the presence of hydrogen bromide is discussed on the ground of the experimental data. This first paper deals with α, β-disubstituted ethenoid compounds, such as cinnamic acid, *m*-nitrocinnamic acid, *p*-methoxycinnamic acid, maleic acid, citraconic acid, crotonic acid, stilbene, and ω-nitrostyrene. The two substituted cinnamic acids, *p*-methoxycinnamic acid with an electron donative methoxyl group, and *m*-nitrocinnamic acid with an electron attractive nitro group, are both unreactive to the mixture of hydrogen bromide and oxygen at room temperature. The former has been found to have an antioxidant action by itself. When *p*-methoxycinnamic acid was added to the solution of cinnamic acid in carbon tetrachloride, it suppressed the reaction of cinnamic acid with the mixture of hydrogen bromide and oxygen to some extent. This may be attributed to the fact that the substitution reaction of *p*-methoxycinnamic acid with bromine atom may take place rapidly, stopping the chain reaction by bromine atom.

The general scheme of the action of hydrogen bromide and oxygen on ethenoid compounds has been discussed by Y. Urushibara[7a] and O. Simamura[7b] and by F. F. Rust and W. E. Vaughan[8], and is supposed to be as follows.

1) olefin + oxygen + hydrogen bromide $\longrightarrow$ Br· (initiations)



9) $Br\cdot + Br\cdot \longrightarrow Br_2$ (termination)

However, this scheme, applied to the reaction of cinnamic acid with hydrogen bromide and oxygen, may not give a satisfactory explanation of our experimental results. If it is assumed that all cinnamic acid dibromide is produced as a chain termination product

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[4] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[5] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

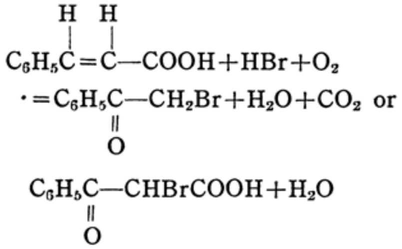
[6] M. R. Anderson, Jr., H. A. Scheraga and Erwin R. VanArtsdalen, *J. Chem. Phys.* **21**, 1258 (1953).

[7a] Y. Urushibara, *Kagakusoho*, Vol. **6**, (1944).

[7b] O. Simamura, This Bulletin, **17**, 326 (1942).

[8] F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **7**, 491 (1942).

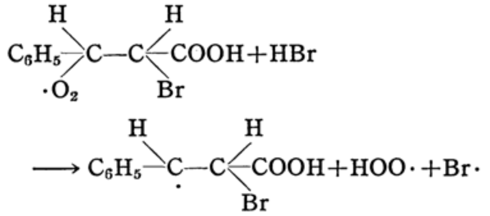
as in the above mechanism, one mole of bromine would be required to produce one mole of cinnamic acid dibromide, and in order to obtain one mole of bromine, at least one mole of cinnamic acid would be consumed by the reaction with one mole of oxygen molecule giving some oxidized product of cinnamic acid. That is, according to the above mechanism, one cycle of propagation reaction would involve only the reaction of one mole of cinnamic acid with one mole of oxygen molecule giving one mole of bromine as cinnamic acid bibromide or as free bromine molecule. Furthermore, in order to obtain one mole of ω-bromoacetophenone, one mole of cinnamic acid and one mole of oxygen molecule would be consumed giving no excess bromine.



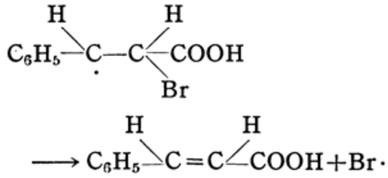
$$C_6H_5\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-COOH+HBr+O_2 \cdot=C_6H_5\underset{\underset{O}{\|}}{C}-CH_2Br+H_2O+CO_2 \text{ or } C_6H_5\underset{\underset{O}{\|}}{C}-CHBrCOOH+H_2O$$

(stoichiometrically)

Our semi-quantitative experiment on the reaction of cinnamic acid with the mixture of hydrogen bromide and oxygen gives some evidence suggesting that the above scheme is not sufficient. The amount of cinnamic acid dibromide produced from 0.0187 mol. of cinnamic acid was 0.0101 mol. (53.4 mol. percent) and that of ω-bromoacetophenone was 0.0048 mol. (25.6 mol. percent for cinnamic acid used). The amount of carbon dioxide evolved was 0.0006 mol. It is noted that the amount of carbon dioxide in mole was not the same as that of ω-bromoacetophenone. This fact suggests the presence of the unstable compound $C_6H_5\underset{\underset{O}{\|}}{C}CHBrCOOH$ in the reaction product. Although the fate of the residual cinnamic acid of about 20% is not ascertained now, neither bromohydroxycinnamic acid nor dihydrocinnamic acid were found in any detectable amount in the reaction products. These compounds, if they existed, would suggest some other process of the formation of bromine from hydrogen bromide. Here, in order to give a reasonable explanation on the experimental result that cinnamic acid dibromide is produced in the yield of more than fifty percent, the following process is proposed in addition to the above ones:

4) 

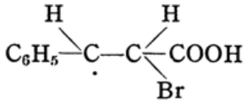
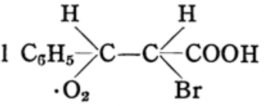
$$C_6H_5\overset{H}{\underset{\cdot O_2}{C}}-\overset{H}{\underset{Br}{C}}-COOH+HBr \longrightarrow C_6H_5\overset{H}{\underset{\cdot}{C}}-\overset{H}{\underset{Br}{C}}-COOH+HOO\cdot+Br\cdot$$

10) 

$$C_6H_5\overset{H}{\underset{\cdot}{C}}-\overset{H}{\underset{Br}{C}}-COOH \longrightarrow C_6H_5\overset{H}{C}=\overset{H}{C}-COOH+Br\cdot$$

or succeeded by the reactions 3), 7) or 8).

11) $HOO\cdot+3HBr \longrightarrow 2H_2O+3/2Br_2$ (overall reaction)

This reproduction process of α-bromocinnamic acid radical  $C_6H_5\overset{H}{\underset{\cdot}{C}}-\overset{H}{\underset{Br}{C}}-COOH$ from the peroxy radical  $C_6H_5\overset{H}{\underset{\cdot O_2}{C}}-\overset{H}{\underset{Br}{C}}-COOH$ (the reaction 4) makes it possible to produce bromine atoms without oxidation of α-bromocinnamic acid radical. The possibility of such a reversal reaction was suggested by R. F. Brown and F. Daniel[9] in their study of the reaction of cinnamic acid with bromine molecule. If it is assumed that such a process takes place actually, this may be an example of sensitization of oxygen by free radical process.

While the mechanism of the initiation reaction is not yet clear, the author will give some fuller suggestion in a later paper. Here it is to be remembered that catechol suppresses the reaction of cinnamic acid with oxygen and hydrogen bromide incompletely. This incompleteness of the antioxidant action of catechol in the presence of an excess of oxygen suggests that catechol cannot inhibit the initiation reaction. Nitrobenzene was found to have no action as an antioxidant in the reaction of cinnamic acid with hydrogen bromide and oxygen, while it is known that it has an inhibiting action in the polymerization reaction. This may be explained by the fact that nitrobenzene does not react with bromine atoms very rapidly.

In the reaction products of crotonic acid with the mixture of hydrogen bromide and oxygen, carbon dioxide and an irritating aldehyde are found in addition to β-bromobutyric acid, α,β-dibromobutyric acid, α-

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[9] R. F. Brown and F. Daniels, *J. Am. Chem. Soc.*, **62**, 2820 (1940).

hydroxy-β-bromobutyric acid which were already described by O. Simamura[1]. The aldehyde gave 2,4-dinitrophenylhydrazone containing bromine and was not identified with the supposedly probable aldehyde, α-bromopropionaldehyde, which gave a 2,4-dinitrophenylhydrazine derivative containing no bromine. At present, the quantitative estimation of these compounds is difficult, so that the material balance in the reaction is not discussed here.

The reaction of maleic acid with hydrogen bromide and oxygen was confusing. The reaction gave a small amount of carbon dioxide. The author at first considered that carbon dioxide was an oxidation product of maleic acid produced in nearly the same way as from cinnamic acid. However, the acid gave carbon dioxide in the reaction with hydrogen bromide in the absence of oxygen, so that it is considered that the acid was decarboxylated through the ionic or any molecular process. It is known that maleic acid adds almost no bromine molecule at room temperature. Citraconic acid gave no reaction product except citraconic anhydride with the mixture of hydrogen bromide and oxygen. These experiments with maleic acid and citraconic acid show that ethenoid α,β-dicarboxylic acids do not react with the mixture of hydrogen bromide and oxygen, due to the stabilization of the ethylenoid double bond by two carboxyl groups.

The reaction of hydrogen bromide and oxygen with stilbene was already studied by O. Simamura[2], and he decribed the formation of stilbene dibromide and an oily product. The present author found a bromophenol and a carbonyl compound in the oily product in addition to a very small amount of carbon dioxide, but the identification of the phenol and the carbonyl compound has not yet been successful. The yield of stilbene dibromide was about 25 mol. percent of the stilbene used. The mechanism of the formation of a phenol from stilbene will be discussed in a later paper concerning the mechanism of the reaction of diphenylethylene with the mixture of hydrogen bromide and oxygen.

The reaction of ω-nitrostyrene with hydrogen bromide appears to be remarkably different from those of the other olefinic compounds. It gave a bromine atom by the action of hydrogen bromide in the absence of oxygen. No influence of oxygen was observed here. M. Takebayashi[10] described a similar action of nitroethylene on hydrogen bromide. ω-Nitrostyrene gave hydroxylamine, ammonia, ω-nitrostyrene dibromide, and an oily substance which was not identified until the present. The reaction mechanism will be discussed in future, when the reaction products have been analysed completely.

Experimental

Materials.—Hydrogen bromide was prepared by the three following methods. a) Bromine was dropped from a dropping funnel into tetralin with gentle heating, and the produced hydrogen bromide was passed through tetralin, anthracene, and phosphorus pentoxide. This method was adopted at first, but hydrogen bromide thus prepared was found to contain a small amount of carbon dioxide, which was presumably produced by the decomposition of some impurities such as tetralin hydroperoxide. b) Bromine was dropped on wet red phosphorus, and the produced hydrogen bromide was purified as in (a). The hydrogen bromide thus produced contained no carbon dioxide, but the production of hydrogen bromide was not smooth enough and the yield was small. c) Hydrogen and bromine were combined directly according to "Org. Synth"[11]. The tank hydrogen dried with phosphorus pentoxide was mixed with bromine, and the mixture was heated by a gentle flame. The hydrogen bromide was passed through copper turnings under a slightly reduced pressure applied to the outlet of the reaction vessel by a Mariot bottle.

Oxygen was obtained from a tank, and passed through aqueous alkali and over phosphorus pentoxide.

Benzene and carbon tetrachloride were purified and dried according to "Org. Solvents,"[12] and distilled.

Cinnamic acid obtained from a commercial source was recrystallized from ethyl alcohol, and kept for a time in an evacuated desiccator, m.p. 133°C.

p-Methoxycinnamic acid was synthesized from anisaldehyde and malonic acid in the presence of ammonia, m.p. 173–4°C.

m-Nitrocinnamic acid was synthesized from *m*-nitrobenzaldehyde according to "Org. Synth."[13], m.p. 196–7°C. Crotonic acid and maleic acid were commerical products. Maleic acid was recrystallized from a mixture of ether and acetone, m.p. 130°C.

Citraconic acid was obtained by pyrolytic distillation of citric acid through citraconic anhydride. ω-Nitrostyrene was synthesized from benzaldehyde and nitromethane, m.p. 58°C.

Stilbene was synthesized by the reduction of benzoin according to "Org. Synth."[14] and recrystallized from ethyl alcohol, m.p. 120°C.

Reactions.—Reaction of Cinnamic Acid with Hydrogen Bromide and Oxygen.—Cinnamic

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[10] M. Takebayashi, *J. Chem. Soc. Japan*, **64**. 192 (1942).

[11] "Organic Syntheses", Collective Vol. 2, John Wiley & Sons, Inc., p. 339.

[12] A. Weissberger and E. Proskauer, "Organic Solvents", Oxford University Press, pp. 105, 156.

[13] "Organic Syntheses", Collective Vol. 1, John Wiley & Sons, Inc., p. 398.

[14] ibid., Vol. 23, p. 86.

acid (0.0187 mol.) was weighed and put together with 30 ml. of carbon tetrachloride, and the dry mixed gas of hydrogen bromide and oxygen was passed through the suspension at room temperature for about 230 minutes. The reaction gas was passed through a calcium chloride tube, over water to absorb hydrogen bromide, and through a barium hydroxide solution. The precipitated barium carbonate was collected on a glass filter, and weighed. About 0.0006 mol. of carbon dioxide was produced from 0.0187 mol. of cinnamic acid. In the reaction vessel about 2.953 g. of a solid matter were deposited, and this matter was proved to be almost pure cinnamic acid dibromide by melting point measurement and analysis of bromine. The carbon tetrachloride solution gave 3.8 g. of a mixture of oil and solid mattter on evaporation at atmospheric pressure. The oil and solid matter were separated on a glass filter. The solid, weighing 0.146 g., melted at 195°C. without recrystallization and was identified with cinnamic acid dibromide. The light-greenish oil weighed 2.23 g. and had an irritating smell. 0.318 g. of the oil was added to a solution of 0.4 g. of 2, 4-dinitrophenylhydrazine prepared according to R. L. Shriner[15]. Rapid formation of a dinitrophenylhydrazone was observed but the mixture was left overnight. The collected 2, 4-dinitrophenylhydrazone weighed 0.257 g., which corresponded to 1.8 g. (0.0048 mol.) of the hydrazone to the total amount of the oil. The 2, 4-dinitrophenylhydrazone melted at 214–6°C and contained 21.1% of bromine (Calcd. for $C_{14}H_{11}O_4N_4Br_2$: Br, 21.1 %). It was identified with the 2, 4-dinitrophenylhydrazone of ω-bromoacetophenone by a mixed melting point with an authentic specimen. In addition to cinnamic acid dibromide and ω-bromoacetophenone, a small amount of an unidentified substance was obtained, but no dihydrocinnamic acid (m.p. 47°C), bromohydroxycinnamic acid (m.p. 120°, 156°, 164°C) nor any other acidic substance were found in the reaction mixture. The total amount of cinnamic acid dibromide was 3.099 g. (0.0101 mol.) which corresponded to 53.4 mol. percent of cinnamic acid used. The substance was dried in a desiccator to constant weight. Two more experiments on the reaction of cinnamic acid with hydrogen bromide and oxygen under the same conditions gave similar results. The amounts of cinnamic acid dibromide produced did not differ by more than 0.3 g.

The Reaction of Cinnamic Acid with Hydrogen Bromide and Oxygen in the Presence of Catechol.—Two solutions of cinnamic acid (3.0 g.) in 40 ml. of carbon tetrachloride were prepared, 0.1 g. of catechol being added to one. Both the solutions were subjected to the action of hydrogen bromide and oxygen at the same time. For the solution containing catechol, carbon dioxide was not evolved, and cinnamic acid was recovered, and no 2, 4-dinitrophenylhydrazone was precipitated with the 2, 4-dinitrophenylhydrazine. From the other solution, carbon dioxide was evolved, and cinnamic acid dibromide was obtained.

Effect of Nitrobenzene.—In 40 ml. of carbon tetrachloride containing 1 ml. of nitrobenzene, 2.01 g. of cinnamic acid were added and the mixture of hydrogen bromide and oxygen was passed through the solution for 535 minutes. Carbon dioxide and cinnamic acid dibromide were obtained and no antioxidant effect of nitrobenzene was observed.

Reactions of *p*-Methoxycinnamic Acid and of *m*-Nitrocinnamic Acid with Hydrogen Bromide and Oxygen.—Hydrogen bromide and oxygen were pased through a solution of *p*-methoxycinnamic acid (3.0 g.) in 40 ml of carbon tetrachloride for 310 minutes. Evolution of carbon dioxide did not take place, and *p*-methoxycinnamic acid was recovered. When hydrogen bromide and oxygen were passed through a solution of 2 g. cinnamic acid and 0.021 g. of *p*-methoxycinnamic acid in 30 ml. of carbon tetrachloride for 265 minutes, a small amount of carbon dioxide was produced, and the reaction product consisted mainly of cinnamic acid dibromide. When 2 g. of cinnamic acid and 2 g. of *p*-methoxycinnamic acid dissolved in 30 ml. of carbon tetrachloride were subjected to the action of hydrogen bromide and oxygen for 405 minutes, a very small amount of carbon dioxide was produced during the passage of the mixed gas, but almost all cinnamic acid and *p*-methoxycinnamic acid were recovered from the carbon tetrachloride solution as a mixture.

Hydrogen bromide and oxygen were passed through a suspension of 2.0 g. of *m*-nitrocinnamic acid in 30 ml. of benzen for 310 minutes at room temperature. *m*-Nitrocinnamic acid was recovered completely without evolution of carbon dioxide.

Reaction of Crotonic Acid with Hydrogen Bromide and Oxygen.—In 50 ml. of carbon tetrachloride 10 g. of crotonic acid was added and the mixture of hydrogen bromide and oxygen was passed through the solution at room temperature for 265 minutes. The carbon dioxide formed was caught as barium carbonate, which weighed 0.215 g. (0.001 mol.). On the bottom of the vessel an oily product deposited from the carbon tetrachloride solution, and, on being kept in a refrigerator, gave a crystalline mass which melted at 95°C. and was identified with α-hydroxy-β-bromobutyric acid. The oil separated from the crystalline mass reduced Fehling's solution at room temperature and gave a small amount of 2, 4-dinitrophenylhydrazone, m.p. 180–200°C. The purification of the hydrazone by either recrystallization or chromatography was unsuccessful. The carbon tetrachloride solution gave about 15 g. of an oil on evaporation. The oil was distilled under a reduced pressure of 20 mmHg. The first fraction which boiled at 48–100°C under that pressure was crotonic acid, the second fraction (1.5 g.) which boiled at 125–130°C was β-bromobutyric acid, and the third fraction (6.5 g.) which passed over at 135–148°C solidified for the most part and the solid melted at 86–88°C. In the flask remained some residue, which melted at 86–88°C. It was identified with crotonic acid dibromide. The velocity of hydrolysis of the second fraction was compared with those of α-bromo- and β-bromobutyric acids. Each compound was weighed into

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15) R.L. Schriner and R.C. Fuson, "The Systematic Identification of Organic Compounds", John Wiley & Sons, Inc., p. 171.

a flask, and 2.0 ml. of a 5.9 N NaOH solution was added. After standing for one hour at room temperature the mixture was neutralized with nitric acid, silver nitrate was added, and the precipitated silver bromide was weighed. α-Bromo- and β-bromobutyric acids liberated 2.6 and 70% of bromine, respectively. The second fraction of the distillation was hydrolysed under the same condition to the extent of 68% and was thus proved to be composed of β-bromobutyric acid. Every fraction gave a positive reaction with Fehling's reagents, and gave a small amount of a 2, 4-dinitrophenylhydrazone suggesting a contamination with some aldehyde, the identification of which was not successful.

Reaction of Maleic Acid with Hydrogen bromide and Oxygen.—Hydrogen bromide and oxygen were passed through a solution of 3.000 g. (0.026 mol.) of maleic acid in 50 ml. of carbon tetrachloride for 315 minutes at room temperature, and 0.0008 mol. of carbon dioxide and 3.199 g. of a precipitate were obtained. The carbon tetrachloride solution gave almost no residue on evaporation. The precipitate showed a large range of melting points. From the precipitate 1.00 g. was sampled and 20 ml. of distilled water was added to it. The water-insoluble part was very small in quantity and it was found to be fumaric acid by a melting point measurement. The water-soluble part was extracted with 20 ml. of ether twice, but both the ethereal extract and the aqueous solution contained maleic acid contaminated with some unidentified compound containing bromine. Formerly the author considered that the carbon dioxide was produced by the free radical mechanism, but, the recent experiment on the reaction of maleic acid with hydrogen bromide in the absence of oxygen showed that carbon dioxide was formed in nearly the same order of amount as in the presence of oxygen. Namely a carbon tetrachloride solution containing 3.00 g. of maleic acid gave about 0.0004 mol. of carbon dioxide on passing hydrogen bromide for 270 minutes at room temperature. Furthermore, when 3 g. of maleic acid with 0.05 g. of catechol was dissolved in 40 ml. of benzene, and hydrogen bromide and oxygen were passed for 165 minutes, 0.0005 mol. of carbon dioxide as barium carbonate was formed.

Reaction of Citraconic Acid with Hydrogen Bromide and Oxygen.—In 60 ml. of benzene 5.0 g. of citraconic acid was dissolved, and the mixture of hydrogen bromide and oxygen was passed through the solution for 360 minutes at room temperature. During the reaction no evolution of carbon dioxide was observed. After evaporation of the reaction mixture, the residual oil was distilled under a reduced pressure of 18 mmHg. and nearly the whole distilled at 98–100°C. The distillate contained no bromine and was identified with citraconic anhydride.

Reaction of Stilbene with Hydrogen Bromide and Oxygen.—To 70 ml. of carbon tetrachloride 5.0 g. (0.028 mol.) of stilbene was added and the mixture of hydrogen bromide and oxygen was passed through the solution for 330 minutes at 19.0°C. Carbon dioxide produced from stilbene was caught in the form of barium carbonate which weighed 0.092 g. (0.00047 mol.). In the reaction vessel a colorless precipitate was deposited from the carbon tetrachloride solution of red color. The deposit weighed 2.73 g. and was found to be composed of stilbene dibromide, m. p. 237°C. It corresponds to 25 mol. percent of the stibene used. The carbon tetrachloride solution was divided into two parts, 44 ml. and 20 ml. The former was shaken with 50 ml. of a 1 N sodium hydroxide solution twice. The sodium hydroxide solution was saturated with carbon dioxide and the separated oil was extracted with ether. The ethereal extract gave a small amount of a phenolic substance on evaporation which gave a positive test for a phenol with ceric ammonium nitrate, the color being brown. It melted at 75°C, and contained bromine, although its amount was very small and its analysis was not successful. It was presumed to be crude tribromophenol, m. p. 96°C. The aqueous solution, saturated with carbon dioxide and shaken with ether, was acidified with sulfuric acid and extracted with ether, but the extract gave practically no appreciable amount of a residue on evaporation. From the carbon tetrachloride solution, shaken with aqueous sodium hydroxide, an oily matter was obtained on evaporation and was distilled under a reduced pressure. A fraction boiling at 112–118°C under 0.9 mmHg gave a crystalline matter. It was separated from the oily part, and recrystallized from alcohol. The substance melted at about 100°C and contained only 8.6% of bromine. Probably it was not pure enough, but the amount was so small that no further recrystallization was attempted. It was supposedly unchanged stilbene, b. p. 166–7°C under 12 mmHg, m. p. 124°C.

Summary

(1) The reaction of α, β-substituted ethenoid compounds with the mixture of hydrogen bromide and oxygen were studied. In the case of cinnamic acid, a reaction mechanism has been tentatively proposed on the basis of the identfied products and their semi-quantitative estimation. The quantitative study of the reaction of cinnamic acid suggests the possibility that oxygen is sensitized by the presence of some free radical if it is relatively stable.

(2) Some experimental data with crotonic acid, sitlbene, and other compounds were presented. Unfortunately, the analysis of the reaction products has not yet been completed up to the present, so that no detailed discussion on these compounds was attempted. A general discussion on the reactions of ethenoid compounds with the mixture of hydrogen bromide and oxygen will be made in a later paper.

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