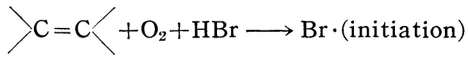
The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds. II[1]

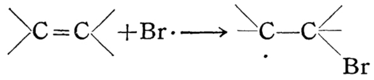
By Makoto Takahasi

(Received August 9, 1956)

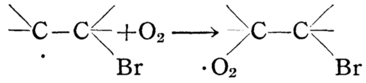
The mechanism of the reactions of the mixture of hydrogen bromide and oxygen with various ethenoid compound has been studied by many workers, and its main character has been elucidated as follows:

(1) 

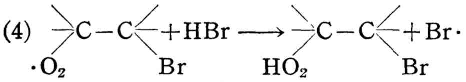
(initiation)

(2) 

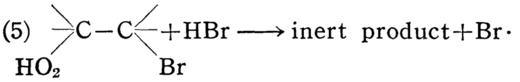
(propagation)

(3) 

(propagation)

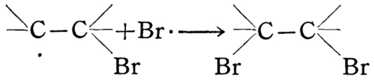
(4) 

(propagation)

(5) 

(propagation)

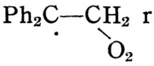
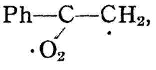
(6) Br·+Br·⟶Br_2 (termination)

(7) 

(termination)

Although the mechanism of the abnormal addition of hydrogen bromide to ethenoid compounds has been established by several workers, the oxidation reaction of ethenoid compounds with oxygen in the presence of hydrogen bromide has not yet been completely elucidated. The mechanism represented above involves several problems to be solved:

(1) The initiation process has been assumed to start by the interaction of an ethenoid compound with hydrogen bromide and oxygen, but it does not mean that a triple collision takes place actually. The process may be composed of at least two steps, but it is not yet determined whether oxygen reacts first with the ethenoid compound and then with hydrogen bromide or vice versa. Consideration of the autoxidation reaction of ethenoid compounds (in the absence of hydrogen bromide) leads to an assumption that oxygen reacts first with the ethenoid compound. But the mechanism of the initiation reaction of autoxidation itself is not clearly known in spite of many discussions. L. Bateman[2] pointed out that the direct olefin-oxygen reaction is so slow that it cannot be hoped that examination of the oxidation product may provide any information on any non-hydroperoxide initiation in the absence of a large amount of inhibitors. The situation, however, is here a little different, because many olefins investigated by the present author have no α-methylene group, so that the oxygen molecule acts on π-electrons of the double bond. Moreover, if the initiation reaction and the propagation reaction give different kinds of products (and the latter a large amount), they may be distinguished by an appropriate analytical method. It is also possible that the ethenoid compound reacts first with hydrogen bromide to form a loose molecular complex, because hydrogen bromide increases the solubility of ethenoid compounds in solvents such as benzene and carbon tetrachloride and there is certain evidence for the formation of complex compounds from aromatic compounds and hydrogen chloride[3].

The formation of small amounts of carbon dioxide and diphenylbromomethane in the reaction of diphenylethylene with hydrogen bromide and oxygen appears to be helpful to the elucidation of the reaction of ethenoid compounds with hydrogen bromide and oxygen. The three following ways of explanation may be possible for the mechanism of the formation of carbon dioxide and diphenylbromomethane. (a) Carbon dioxide and diphenylbromomethane may be formed by an initiation reaction, but not by a propagation reaction. If it is the case, oxygen acts first on the β-carbon atom of diphenylethylene to give  $Ph_2\dot{C}-CH_2O_2$ rather than on the α-carbon atom to give  $Ph-C(\cdot O_2)-\dot{C}H_2$, and the reaction proceeds in the following way:

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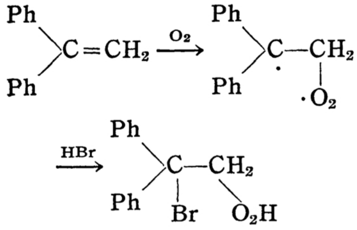
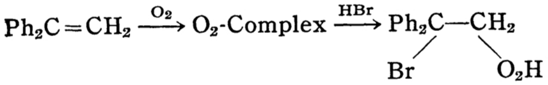
[1] Part I, This Bulletin, **29**, 625 (1956).

[2] L. Bateman, *Quart. Rev.* VIII, 147, (1954).

[3] H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3572 (1952).

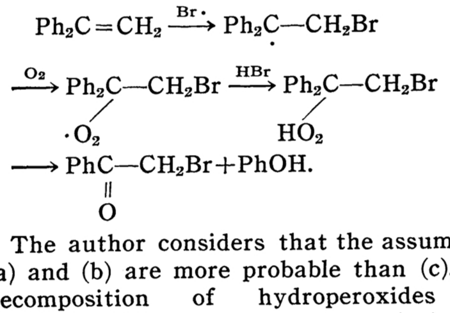


The bromohydroperoxide may decompose to carbon dioxide and diphenylbromomethane through a not yet characterized process in the presence of oxygen and hydrogen bromide. (b) The products are produced by the initiation process as above. But the olefin may form an intermediate complex with oxygen*, and then the complex reacts with hydrogen bromide:



$$\mathrm{Ph_2C=CH_2 \xrightarrow{O_2} O_2\text{-}Complex \xrightarrow{HBr} Ph_2\underset{Br}{C}-\underset{O_2H}{CH_2}}$$

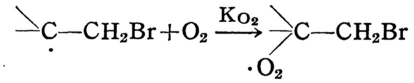
(c) An alternative assumption might be that these products were produced by a propagation reaction, but it is probably far from the fact because diphenylethylene adds the bromine atom at the β-carbon atom more rapidly than at the α-carbon atom due to the stability of $\mathrm{Ph_2\underset{\cdot}{C}-CH_2Br}$ greater than that of $\mathrm{Ph_2BrC-\underset{\cdot}{C}H_2}$. The formation of ω-bromoacetophenone and a phenolic compound in relatively large amounts in the reaction may be explained by assuming a propagation reaction as follows:



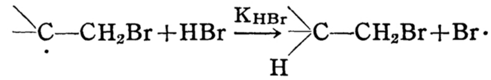
$$\mathrm{Ph_2C=CH_2 \xrightarrow{Br\cdot} Ph_2\underset{\cdot}{C}-CH_2Br \xrightarrow{O_2} Ph_2\underset{\cdot O_2}{C}-CH_2Br \xrightarrow{HBr} Ph_2\underset{HO_2}{C}-CH_2Br \longrightarrow Ph\underset{O}{\underset{\|}{C}}-CH_2Br+PhOH.}$$

The author considers that the assumptions (a) and (b) are more probable than (c). The decomposition of hydroperoxides (e.g. $\mathrm{Ph_2\underset{HO_2}{C}-CH_2Br}$) by hydrogen bromide has not been studied in detail until the present, but it may probably proceed through an acid catalysed mechanism, as suggested by F. F. Rust and W. E. Vaughan[4]. The formation of phenolic substances from diphenylethylene and from styrene is explained by this mechanism.

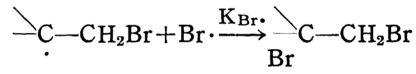
(2) It is impossible to establish completely the scheme of the propagation, chain transfer and termination reactions from the result of the yield of the final products, because the velocity constants of the following most probable competitive processes have not yet been estimated in any case:

(1) 

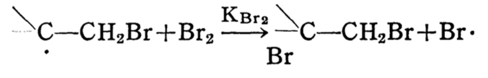
$$>\underset{\cdot}{\mathrm{C}}-\mathrm{CH_2Br}+\mathrm{O_2} \xrightarrow{K_{O_2}} >\underset{\cdot O_2}{\mathrm{C}}-\mathrm{CH_2Br}$$

(2) 

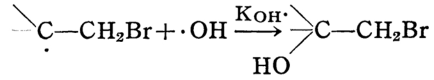
$$>\underset{\cdot}{\mathrm{C}}-\mathrm{CH_2Br}+\mathrm{HBr} \xrightarrow{K_{HBr}} >\underset{H}{\mathrm{C}}-\mathrm{CH_2Br}+\mathrm{Br\cdot}$$

(3) 

$$>\underset{\cdot}{\mathrm{C}}-\mathrm{CH_2Br}+\mathrm{Br\cdot} \xrightarrow{K_{Br\cdot}} >\underset{Br}{\mathrm{C}}-\mathrm{CH_2Br}$$

(4) 

$$>\underset{\cdot}{\mathrm{C}}-\mathrm{CH_2Br}+\mathrm{Br_2} \xrightarrow{K_{Br_2}} >\underset{Br}{\mathrm{C}}-\mathrm{CH_2Br}+\mathrm{Br\cdot}$$

(5) 

$$>\underset{\cdot}{\mathrm{C}}-\mathrm{CH_2Br}+\cdot\mathrm{OH} \xrightarrow{K_{OH\cdot}} >\underset{HO}{\mathrm{C}}-\mathrm{CH_2Br}$$

Generally. the velocity constants of the recombination reactions of the free radical with the bromine atom (3) and with the free hydroxyl radical (5) may be far greater than those of the reactions of the free radical with molecular oxygen (1), with hydrogen bromide (2), and with bromine molecule (4), unless some steric effect modifies the velocity constants, but the concentrations of the bromine atom and of the free hydroxyl radical may be far smaller than those of oxygen, hydrogen bromide and molecular bromine. Although atropic acid gives a large amount of α-hydroxy-β-bromohydratropic acid, it is improbable from the reason stated below that the product is yielded by the reaction of free radical $\mathrm{Ph\overset{HOOC}{\underset{\cdot}{C}}-Ch_2Br}$ with free hydroxyl radical. A comparison of the velocity constants of the reactions (1), (2) and (3) is also impossible now. It seems probable that the reactivity of the free radical with hydrogen bromide depends upon the stability of the free radical, and that the velocity constant K_{O_2} is in general greater than K_{HBr}, considering that many compounds such as cinnamic acid, atropic acid, and diphenylethylene, which give free radicals stabilized by conjugation, give various oxygenated compounds but not hydrogen bromide adducts in spite of the presence of a large amount of hydrogen bromide. The comparison of the velocity constants K_{O_2} and K_{HBr} has an important meaning in considering the reaction mechanism discussed here. It is known that the bromine addition reaction of cinnamic acid is inhibited by the presence of oxygen,

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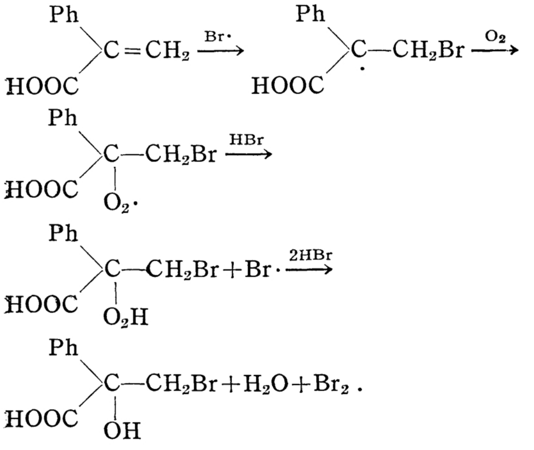
* There is an indication that aromatic compounds form complex compounds with oxygen. D. F. Evans, *J. Chem. Soc.*, **1953**, 345.

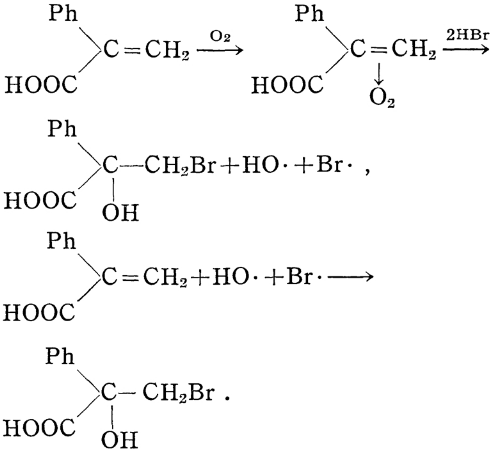
[4] R. R. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, **41**., 2595 (1949).

but the inhibition seems not to be serious according to our experiment described in the next paper.

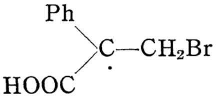
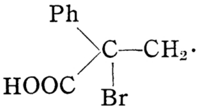
In the previous paper[1] the author emphasized the significance of the material balance in order to discuss the reaction mechanism. Unfortunately, in many cases of the reactions discussed by the author such as those of crotonic acid, diphenylethylene and stilbene, the reaction mixtures are composed of several compounds, which are relatively labile to chromatography, recrystallization and distillation, so that the establishment of the material balance is unsuccessful. Fortunately, in the reaction of atropic acid with hydrogen bromide and oxygen, α-hydroxy-β-bromohydratropic acid (the determination of the structure of the acid is described in the experimental part) was obtained in about 77 mole percent yield of atropic acid. In addition to this a very small amount of ω, ω-dibromoacetophenone and carbon dioxide and bromine were obtained. These products may be derived by the initiation reaction or a side reaction, but the details of the mechanism is not clear. Atropic acid which gives neither a hydrogen bromide adduct nor atropic acid dibromide is clearly distinguished from cinnamic acid giving more than fifty mole percent of cinnamic acid dibromide and about 25 mole percent of ω-bromoacetophenone under the same conditions. If α-hydroxy-β-bromohydratropic acid was formed by the following process,



bromine should be produced in moles equal to α-hydroxy-β-bromohydratropic acid, but actually only a small amount of free bromine, no appreciable amount of water, and no atropic acid dibromide is found in the reaction products. The necessary condition in considering the reaction mechanism is that the atom which adds first to double bond should attack the β-carbon atom of atropic acid, but not the α-carbon atom, because of the greater stability of the free radical formed. Then the following may be a possible mechanism, which involves no cyclic chain propagation:



The problem, however, will be left unsolved until a kinetic study of these reactions is possible.

G. Merling⁵⁾ asserted, that atropic acid gave β-bromohydratropic acid with hydrobromic acid, while α-bromohydratropic acid was obtained when dry hydrogen bromide was passed through a benzene solution of atropic acid. If such a reversal of the direction of addition of hydrogen bromide to atropic acid should take place, it could not be explained on the grounds of the formation of the more stable free radical in the of reaction of bromine atom with the olefinic compound, because the radical  would be more stable than the other radical 

The author investigated the addition of hydrogen bromide to atropic acid both under oxydant and anti-oxydant conditions, but no reversal was observed.

Experimental

Materials.—Hydrogen bromide and oxygen were prepared and purified as described in the previous paper¹⁾. Diphenylethylene was prepared from bromobenzene and ethyl acetate according to Org. Syntheses⁶⁾, b. p. 123-5°C/mmHg, $n_D^{19^\circ}$ 1.6084, $n_D^{9.6^\circ}$ 1.6135. Atropic acid was prepared by the hydrolysis of acetophenone cyanohydrin and recrystallized from benzene, m. p. 106°C. Styrene, a

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5) G. Merling, *Ann.*, **209**, 1 (1881).

6) "Organic Syntheses", Collective Vol. I, John Wiley & Sons, Inc., p. 221.

commercial product, was washed with alkaline water, dried with calcium chloride and distilled under reduced pressure with a fractionation column.

TABLE I

THE REACTION OF DIPHENYLETHYLENE WITH HYDROGEN BROMIDE AND OXYGEN

No.	Diphenyl-ethylene g. (mol.)	Solvent ml.	Reagents	Time Min.	Products					
					CO_2 mm. mol.	Ph_2CHBr	$PhCOCH_2Br$	PhOH mm. mol.	Ph_2CBrCH_2Br	$Ph_2C=CH_2$
1	2(0.011)	Benzene 70	$HBr+O_2$	180	0.9	+	Not investigated	Not investigated	?	?
2	2	〃 30	〃	70	0.7		Purification unsuccessful			
3	2	〃 30	〃	105	0.8	+	?	?	?	?
5	3.51(0.0195)	〃 40	〃	100	0.6	?	?	5	?	+
6	10(0.0056)	CCl_4 70	〃	215	0.6	?	?	6	?	+
7	10	〃 70	〃	360	0.8	?	?	7	+	+

"?" Means that its existence was not ascertained, but it is most probable.
"+" Means that its existence was ascertained qualitatively.
"−" Means that its absence was ascertained.

Reaction of Diphenylethylene with Hydrogen Bromide and Oxygen.—The mixture of hydrogen bromide and oxygen was passed into a solution of diphenylethylene in benzene or in carbon tetrachloride for several hours. The results of experiments under various conditions are summarized in Table I and details will be described below. a) Identification of diphenylbromomethane. The reaction mixture of Exp. 1. was washed with water, and dried with anhydrous sodium sulfate. When benzene was removed by distillation, a light yellow oil was obtained. The oil was heated with a few ml. of water in a sealed tube at 150°C for about four hours. After cooling, the sealed tube was opened, and a mixture of an oil and a crystalline mass was obtained. The crystalline mass was separated and recrystallized from petroleum ether, m. p. 120°C. It contained no bromine and was identified as dibenzhydrylether ($((C_6H_5)_2CH)_2O$ by a mixed melting point. The authentic dibenzhydrylether was synthesized from diphenylbromomethane by heating it with water in the same way. An attempted separation of diphenylbromomethane itself in Expt. 6 by distillation under reduced pressure was rendered unsuccessful by the presence of a large amount of unchanged diphenylethylene. b) Identification of ω-bromoacetophenone. In Expt. 5 the oil was kept in an electric refrigerator, giving a mixture of an oil and a crystalline mass. The crystalline mass was separated on a glassfilter, and weighed about 0.4 g., m. p. 52°C., and it was identified as ω-bromoacetophenone, by a mixed melting point and by the preparation of 2, 4-dinitrophenylhydrazone, m. p. 214–216°C. d) Identification of phenol. When the reaction mixture was shaken with water or alkaline water, and a bromine-potassium bromide solution was added to the aqueous extract, tribromophenol was precipitated. Furthermore, when the alkaline extract was saturated with carbon dioxide and extracted with ether, about 2 g. of a phenolic oil were obtained. From the oil about 1.45 g. of phenyl benzoate was obtained by treating it with benzoyl chloride (Expt. 7). Unfortunately, the separation of these products from the reaction mixture of one experiment using 10 g. of diphenylethylene was unsuccessful. When 10 g. of diphenylethylene were used, the feature of the reaction was a little different. (Expt. 6 and 7) The amount of carbon dioxide was nearly in the same order. When the carbon tetrachloride solution was shaken with 1 N NaOH solution once and with 100 ml. of distilled water dried with anhydrous sodium sulfate, and distilled under reduced pressure, it gave the three following fractions, b.p. 82–88°C/0.9 mmHg, and 100°C/1 mmHg and the residue. The first fraction ($n_{\mathrm{D}}^{9.6^\circ}$ 1.6182) contained no bromine and was found to be mainly composed of unchanged diphenylethylene, ($n_{\mathrm{D}}^{9.6^\circ}$ 1.6135). The second fraction solidified and was recrystallized from petroleum ether, m. p. 38°C.

Anal. Found: Br, 30.9. Calcd. for $(C_6H_5)_2CCHBr$: Br, 30.9%.

These results suggest that a large amount of diphenylethylene does not react with the mixture of hydrogen bromide and oxygen due to the accumulation of a phenolic substance in the reaction mixture. β-Bromodiphenylethylene may be derived from α, β-dibromodiphenylethane during distillation, for the latter is very sensitive to heat.

Reaction of Atropic Acid with Hydrogen Bromide and Oxygen.—Experimental results are summarized in Table II. Expt. 59 was carried out as following: Atropic acid (5 g., 0.034 mol.) was dissolved in 50 ml. of carbon tetrachloride and the mixture of hydrogen bromide and oxygen was passed into the solution for 300 min. at room temperature. The solution turned red during the reaction. It was kept over-night in an electric refrigerator, giving 2 g. of a crystalline mass, which was recrystallized from benzene to colorless crystals, m. p. 115°C. The substance was acidic, and found to be α-hydroxy-β-bromohydratopic acid as described below.

The carbon tetrachloride solution was washed twice with distilled water, and the aqueous solution was extracted with ether. The ethereal extract gave about 2 g. of the same acid, m. p.

TABLE II

THE REACTION OF ATROPIC ACID WITH HYDROGEN BROMIDE AND OXYGEN

					Products				
No.	Atropic Acid, g. mol.	Solvent, ml.	Reagent	Reaction Time Min.	CO_2 mm mol.	Br_2 mm mol.	$PhCCH_2Br$ HOOC OH mm mol.	$PhCHCH_2Br$ HOOC mm mol.	$PhCOCHBr_2$
48	1	CCl_4 30	$HBr+O_2$	230	1.3				
52	1.5 (0.01)	〃 30	N_2 HBr	60 290	None			6.5	
53	1.5	〃 30	Benzoyl Peroxide, 30 mg. HBr	295	〃			5.7	
55	5.00 (0.034)	〃 50	$HBr+O_2$	325	5.3	1.45	18		+
58	〃	〃 50	〃	300	3.5		19		+
59	〃	〃 50	〃	300	3.4	0.25	25		+
56	0.2	Benzene 20	(O_2 for a short time) HBr	180	—	—	—	Oily product	
57	0.2	〃 30	HBr Catechol 10 mg.	195	—	—	—	+	

115°C. The carbon tetrachloride solution was then shaken twice with 50 ml. of 1 N aqueous sodium hydroxide, and the alkaline solution was acidified with hydrochloric acid and extracted with ether. The ethereal extract gave about 0.9 g. of the same acid. Thus about 6.1 g. (0.026 mol. as calculated for α-hydroxy-β-bromohydratropic acid) of the acid, m. p. 115°C, was obtained from 5 g. (0.034 mol.) of atropic acid. The carbon tetrachloride solution was then dried with anhydrous sodium sulfate, and evaporated under reduced pressure, when a small amount of a precipitate and 0.94 g. of an oil were left. The oil (0.78 g. of the oil in ethyl alcohol) and 2,4-dinitrophenylhydrazine gave a precipitate weighing 0.377 g. It was separated into parts soluble and insoluble in hot chloroform. The former was a yellow crystalline substance, which melted at 178–180°C after one recrystallization from chloroform.

Anal. Found: C, 38.27; H, 2.51; N, 12.7; Br, 33.5. Calcd. for $C_{14}H_{10}O_4Br_2$: C, 36.71; H, 2.20; N, 12.2; Br, 34.9%.

The latter was an orange crystal, insoluble in any solvents available, contained no bromine, and melted at about 200°C. Its amount was very small, so that its identification was unsuccessful. ω, ω-Dibromoacetophenone itself also gave two species of products with 2,4-dinitrophenylhydrazine, which appeared to be the same substances as those obtained above. The 2,4-dinitrophenylhydrazone, m. p. 178–180°C was identified with the 2,4-dinitrophenylhydrazone of ω, ω-dibromoaceotophenone by mixed melting point and by comparison of their infrared spectra as shown in Fig. 1 and 2, although the analytical results did not give a good agreement as 2,4-dinitrophenylhydrazone of ω, ω-dibromoacetophenone $C_{14}H_{10}O_4Br_2$, because the amount of the sample was so small that it could not be repeatedly recrystallized.

The acid, m. p. 115°C, had a neutralization equivalent of 244, and its composition was as follows:

Anal. Found: C, 44.9; H, 3.92; Br, 32.0. Calcd. for $C_9H_9O_3Br$: C, 44.1; H, 3.67; Br, 32.3%.

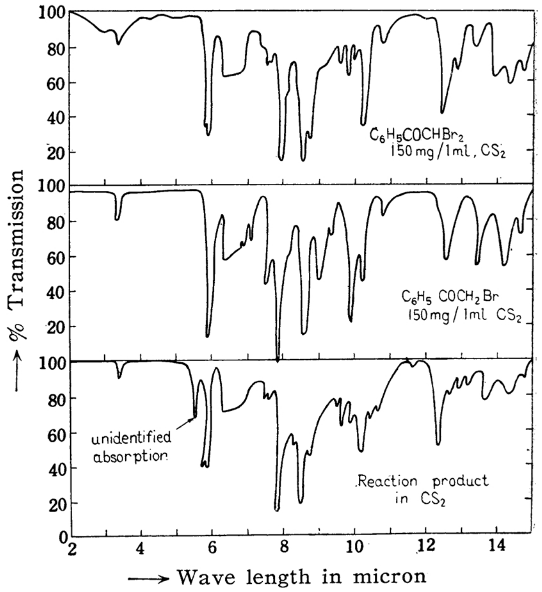

Fig. 1. Infrared spectra of two ketones and of reaction products (Expt. 59).

This indicates that the acid is either α-hydroxy-β-bromo- or α-bromo-β-hydroxyhydratropic acid. The positions of the hydroxyl group and the bromine atom were determined as follows: Infrared spectrum of the acid appeared to be similar to that of atrolactic acid as shown in Fig. 3. Treatment of the acid with Fenton reagent gave no carbonyl compound. An attempted synthesis of the acid by the reaction of atropic acid with hypobromic acid resulted in the formation of only a polymeric substance containing no bromine. However, when it was brought to reaction with lead tetracetate, it gave ω-bomoacetophenone, which resulted from the oxidative scission of α-hydroxy-β-bromohydratropic acid, because it was reported that[7], when an α-hydroxycarboxylic acid is treated with lead tetracetate, it gives a carbonyl

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[7] H. Oeda, This Bulletin, 9, 8 (1934).

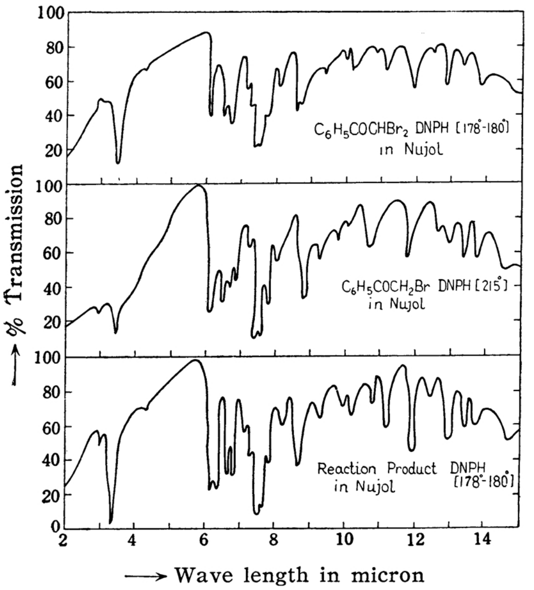


Fig. 2. Infrared spectra of 2, 4-dinitrophenylhydrazones (DNPH) of two ketones and of reaction products (Exp. 59).

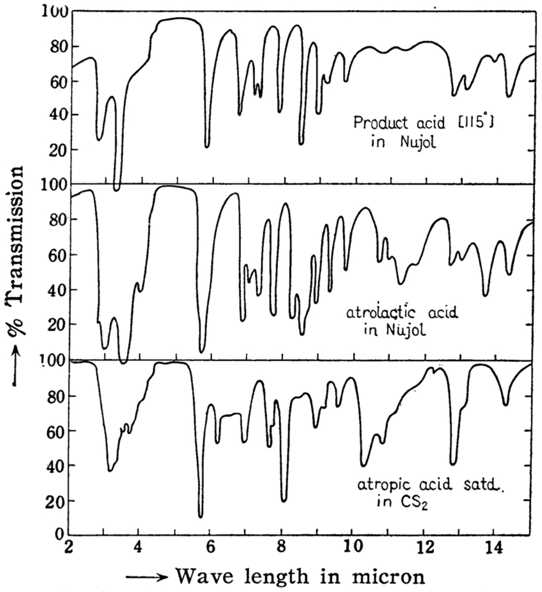
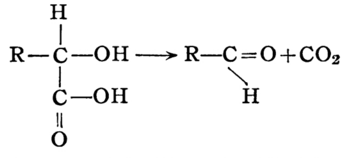


Fig. 3. Infrared spectra of α-hydroxy-β-bromohydratropic acid, atrolactic acid, and atropic acid.

compound and carbon dioxide as follows:



$$\mathrm{R{-}\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle O}{\underset{\|}{C{-}OH}}}{\underset{|}{C}}}}{-}OH \longrightarrow R{-}\underset{\displaystyle \diagdown\, H}{C}{=}O+CO_2}$$

A mixture of 0.236 g. of $Pb(AcO)_4$ and 0.245 g. of the acid, m. p. 115°C, in 3 ml. of benzene was heated at 60–65°C. for 1.5 hr. After it was assured with a KI solution that no unchanged $Pb(AcO)_4$ remained, the yellow precipitate was filtered off. From the benzene solution a highly irritating oil was obtained on removing benzene by distillation. The oil partly solidified when it was kept in a cold place, but, as the amount was very small, the whole was brought to reaction with 2, 4-dinitrophenylhydrazine, giving an orange-colored precipitate. It was recrystallized from chloroform, m. p. 215°C.

Anal. Found: Br, 20.7. Calcd. for 2, 4-dinitrophenylhydrazone of ω-bromoacetophenone, $C_{14}H_{11}N_4O_4Br$: 21.7%.

A mixed melting point showed it was 2, 4-ninitrophenylhydrazone of ω-bromoacetophenone. From these results it was concluded that the acid was α-hydroxy-β-bromohydratropic acid, $C_6H_5C(CH_2Br)(OH)COOH$. This acid did not react with Fenton reagent, probably because of the absence of hydrogen atom at the hydroxylated carbon atom.

Addition of Hydrogen Bromide to Atropic Acid.—In 30 ml. of carbon tetrachloride 1.5 g. of atropic acid was dissolved, and hydrogen bromide was passed into the solution for 290 min. after sweeping the solution by nitrogen. A very small amount of a precipitate was obtained, which did not dissolve in various solvents and melted at 220°C. It contained no bromine and it may be a dimer of atropic acid. The solution was washed twice with distilled water, dried with anhydrous sodium sulfate, and evaporated, giving 1.5 g. of a crystalline substance, which was recrystallized from carbon disulfide, m. p. 96°C.

Anal. Found: Br, 34.1. Calcd. for $C_9H_{10}O_2Br$: Br, 34.9%.

By a mixed melting point, it was found to be β-bromohydratropic acid (Expt. 52.)

Addition of Hydrogen Bromide to Atropic Acid in the Presence of Benzoyl Peroxide.—Into a solution of 1.5 g. of atropic acid and 0.030 g. of benzoyl peroxide in 30 ml. of carbon tetrachloride hydrogen bromide was passed for 300 min. at the room temperature. By the same treatment as described above β-bromohydratropic acid was identified by a mixed melting point (Expt. 53).

The Reaction of Styrene with Hydrogen Bromide and Oxygen.—The mixture of hydrogen bromide and oxygen was passed into a solution of 10.0 g. (0.096 mol.) of styrene in 60 ml. of carbon tetrachloride for 240 min. at 20°C. The amount of carbon dioxide was 0.144 g. as barium carbonate (0.00073 mol.), and the water used to absorb waste hydrogen bromide gave a positive test with Schiff reagent, suggesting the presence of formaldehyde, although its identification was not successful. The carbon tetrachloride solution was washed with 120 ml. of 1 N NaOH, then with 60 ml. of water, and dried with anhydrous sodium sulfate. The alkaline solution was saturated with carbon dioxide, and extracted with ether. The ethereal solution gave a phenolic substance, but its identification was unsuccessful. The neutral oil obtained from the carbon tetrachloride solution was distilled under reduced pressure. The first fraction, which distilled at 58–60°C/3 mmHg weighed about 1.6 g., and was identified as α-bromoethylbenzene, by comparing the refractive index of the oil ($n_D^{12^\circ}$ 1.5642) with that of an authentic specimen ($n_D^{12^\circ}$ 1.5636). The second fraction distilled at 108–110°C/3 mmHg and about 2.3 g. of the distillate solidified and showed a melting point 65°C.

Anal. Found: Br, 61.1. Calcd. for styrene dibromide, $C_8H_8Br_2$: Br, 60.7%. The total amount of styrene dibromide obtained in crystals in this experiment was not less than 4.8 g. (2.3+1.8+0.7). Supposedly the oil separated from the solid styrene dibromide contained yet styrene dibromide. The characteristic feature of the reaction was that a phenolic substance, styrene dibromide, and carbon dioxide were produced. The formation of the phenolic substance may be accompanied by the production of formaldehyde and carbon dioxide. Detailed investigation of the reaction mechanism of styrene with hydrogen bromide and oxygen will be made in future.

Summary

(1) The reaction of diphenylethylene, atropic acid, and styrene with the mixture of hydrogen bromide and oxygen were studied. In the case of diphenylethylene, diphenylbromomethane, ω-bromoacetophenone, diphenylethylene dibromide, phenol and carbon dioxide were obtained as reaction products. A reaction mechanism was proposed to explain how these compounds were produced.

(2) In the case of atropic acid, a large amount of α-hydroxy-β-bromohydratopic acid and a small amount of ω, ω-dibromoacetophenone and of carbon dioxide were obtained. A consideration on the mechanism of the formation of these products was given on the basis of the identified products and their semiquantitative estimation.

(3) Addition of hydrogen bromide to atropic was carried out under various conditions. No reversal of the direction of addition of hydrogen bromide was observed contrary to the previous reference.

(4) The reaction of styrene with the mixture of hydrogen bromide and oxygen added an example yielding a phenolic substance in the reaction.

Tne author wishes to express his hearty thanks to Prof. Y. Urushibara and Prof. O. Simamura for their kind guidance and encouragement throughout this work. The author is indebted to Dr. S. Tanaka for the infrared spectra measurement and their interpretation.

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