The Action of Hydrogen Bromide and Oxygen on Various Ethenoid Compounds. III. The Steric Effects of the Bromo Free Radicals Produced from Various Ethenoid Compounds on the Reactivities with Oxygen

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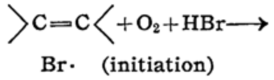
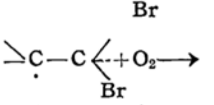
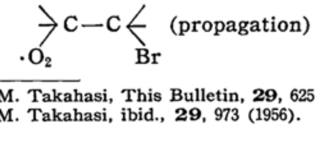
The mechanism of the action of hydrogen bromide on various ethenoid compounds in the presence of a large amount of oxygen has been discussed in the preceding papers of this series[1,2], and the fundamental reaction scheme has been assumed as follows:

(1)

$$>C=C< + O_2 + HBr \longrightarrow Br\cdot \quad \text{(initiation)}$$

(2)

$$>C=C< + Br\cdot \longrightarrow >\underset{\cdot}{C}-\underset{Br}{C}< \quad \text{(propagation)}$$

(3)

$$>\underset{\cdot}{C}-\underset{Br}{C}< + O_2 \longrightarrow \underset{\cdot O_2}{>C}-\underset{Br}{C}< \quad \text{(propagation)}$$

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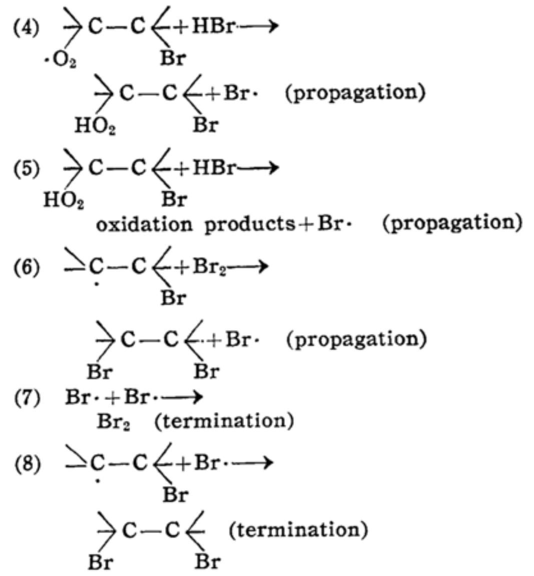
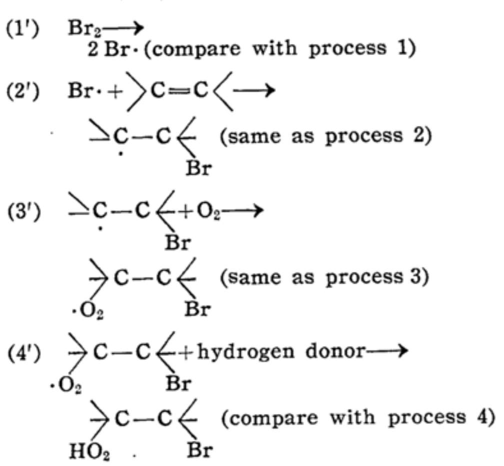
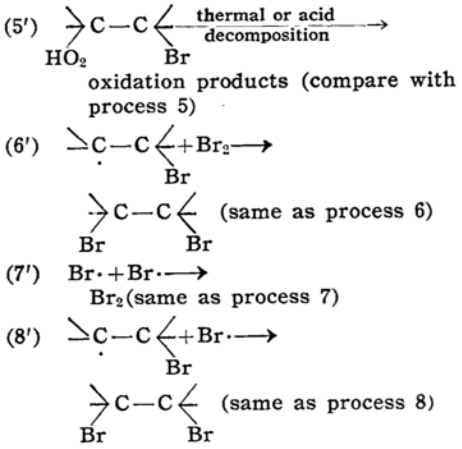
[1] M. Takahasi, This Bulletin, **29**, 625 (1956).

[2] M. Takahasi, ibid., **29**, 973 (1956).

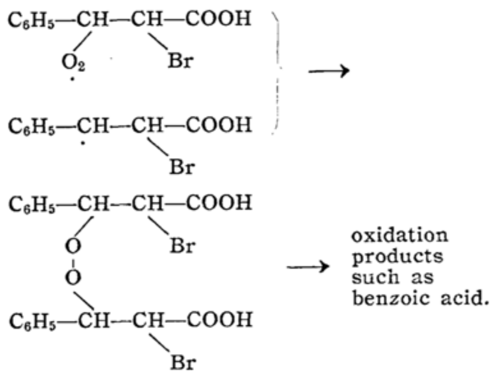


From the kinetical point of view, it is desirable to establish a complete method to determine the velocity constants of these reactions, but at present it may be difficult to carry out a kinetical study of the reactions of the three component systems. The author attempted to study qualitatively the reactions of bromine with ethenoid compounds, such as β-methylcinnamic acid, cinnamic acid, *p*-methoxycinnamic acid, atropic acid, and diphenylethylene, to compare the intermediate bromo free radicals to be produced from these ethenoid compounds in the reactivity with oxygen, expecting that it may be helpful to elucidating the mechanism of the reactions of hydrogen bromide and oxygen with ethenoid compounds, because the reactions are presumed to include the same reaction processes as 2,3,6,7, and 8 as shown below:





If any hydrogen donor such as hydrogen bromide does not exist, reaction 4′ does not proceed, and no bromohydroperoxide is produced. R. F. Brown and F. Daniels[3] observed the rate of the reaction of cinnamic acid with bromine in the absence of a hydrogen donor is reduced by the presence of oxygen in the light, and O. Simamura[4] observed the same effect of oxygen to occur even in the dark. J. L. Magee and F. Daniels[5] ascribed the inhibitive action of oxygen to the reaction of the bromo free radical with oxygen and to the reaction of the bromohydroperoxide radical thus produced with another bromo free radical, giving a peroxide or further oxidation products with evolution of a large amount of heat.



The author attempted to identify the reaction products produced by the reactions of ethenoid compounds with bromine in the presence of an excess of oxygen. The ethenoid compounds, except β-methylcinnamic acid and diphenylethylene, did

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

[4] O. Simamura, This Bulletin, **17**, 274 (1942).

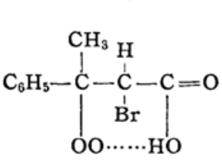
[5] J. L. Magee and F. Daniels, *J. Am. Chem. Soc.*, **62**, 2825 (1940).

not give any appreciable amounts of oxidation products other than dibromides by the reactions with bromine in nonpolar solvents in spite of the presence of a large amount of oxygen, and the inhibitive action by oxygen was not remarkable. However, the reaction of β-methylcinnamic acid with bromine in the presence of a large amount of oxygen manifested a remarkable feature, as described below.

When oxygen was passed through a benzene solution of β-methylcinnamic acid in the sunlight with simultaneous addition of a benzene solution of bromine, the color of bromine faded far less rapidly than without introduction of oxygen. The reaction products were found to consist of carbon dioxide, acetophenone, a small amount of β-methylcinnamic acid dibromide, and some unidentified aldehyde.

Further, the reaction of β-methylcinnamic acid with hydrogen bromide and oxygen was carried out, and the reaction products were found to include carbon dioxide, α-bromoacetophenone and p-bromophenol, and a large amount of β-methylcinnamic acid was recovered, while β-methylcinnamic acid dibromide could not be detected in the products. It is to be noted that the reaction products in this case do not correspond to those of the reaction of cinnamic acid with hydrogen bromide and oxygen[1]. p-Bromophenol formed may inhibit the progress of the reaction of β-methylcinnamic acid with hydrogen bromide and oxygen.

Generally, in the reactions of ethenoid compounds with bromine in the presence of a large amount of oxygen, no hydrogen donor apparently exists. However, if acetophenone is formed in the reaction of β-methylcinnamic acid with oxygen and bromine via a bromohydroperoxide formation, reactions 4′, and 5′, it is necessary to assume the presence of a hydrogen donor. Although no evidence for either an intra- or an inter-molecular hydrogen transfer is available, it seems probable that the hydrogen of the carboxyl group moves to the peroxidic oxygen to give a bromohydroperoxide, considering the relative positions of the carboxyl group and the peroxidic oxygen. The structure of the intermediate was presumed to be



$$C_6H_5-\overset{CH_3}{\underset{OO\cdots}{C}}-\overset{H}{\underset{Br}{C}}-\underset{\cdots HO}{C}=O$$

The special reactivity of β-methylcinnamic acid with oxygen, compared with other ethenoid compounds, may be understandable from following consideration.

The yields of oxidation products in the reactions of the ethenoid compounds with oxygen and bromine are not directly related with the structures of the ethenoid compounds themselves, but depend on the reactivity of the bromo free radicals with oxygen. However, the discussions on the ethenoid compounds as described below may be helpful to understanding the reactivity of the bromo free radicals.

H. Suzuki[6], in his study on the absorption spectra of a series of stilbene derivatives, i.e. stilbene, α-methylstilbene, and α,β-dimethylstilbene, found that the absorption maxima of these compounds are shifted progressively in the order towards shorter wave lengths with increasing angles of twist of the phenyl groups out of the plane of the ethylenic linkage caused mainly by the steric repulsion between the methyl group and the phenyl group attached to different carbon atoms of the ethylenic linkage. In parallel with the study of the steric effect on the ultraviolet absorption spectra, H. Suzuki, O. Simamura and T. Ichihashi[7,8] studied the action of the bromine atom and oxygen on stilbene derivatives, and they found that the action of the bromine atom and oxygen on α,β-dimethylstilbene caused an oxidative cleavage of the double bond.

β-Methylcinnamic acid may be in a state of less steric strain than α,β-dimethylstilbene, because in the former the methyl group interacts only with one phenyl group, and the methyl and the phenyl group are attached to the same carbon atom of the ethylenic linkage. In the latter, the both methyl groups interact with the phenyl groups attached to different carbon atoms respectively, so that it may be in a state of a larger steric strain than β-methylcinnamic acid. Notwithstanding, in the series of cinnamic acid, β-methylcinnamic acid, and β-ethylcinnamic acid, the maxima of the absorp tion spectra are also shifted progressively in the order towards shorter wave lengths with decrease in extinction coefficients, as in the series of stilbene derivatives. This fact may indicate existence of a

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[6] H. Suzuki, This Bulletin, **25**, 145 (1952).

[7] H. Suzuki, O. Simamura and T. Ichihashi, ibid., **27**, 235 (1954).

[8] O. Simamura and H. Suzuki, ibid., **27**, 231 (1954).

steric repulsion between the methyl group and the phenyl group in β-methylcinnamic acid.

The amount of the steric strain of π-electron system caused by the repulsion between the methyl group and the phenyl group may be of the same order in the intermediate bromo free radical from β-methylcinnamic acid as in β-methylcinnamic acid, because the methyl group and the phenyl group are attached to the same carbon atom. Thus the reactivity of the bromo free radical produced from β-methylcinnamic acid with oxygen may be larger than the reactivity of the bromo free radicals produced from cinnamic acid and any other ethenoid compounds with no steric strain.

β-Methylcinnamic acid, α,β-dimethylcinnamic acid and diphenylethylene and the intermediate free radicals therefrom as well may be subject to a large steric strain. In α-methylcinnamic acid, however, the interaction of the α-methyl group with the β-phenyl group will be released at the stage of the intermediate bromo free radical, so that the reactivity of the bromo free radical produced from α-methylcinnamic acid with oxygen may not be large.

An experiment on the reaction of α-methylcinnamic acid with hydrogen bromide and oxygen was attempted, but no reaction took place. On the other hand, the experiment on the reaction of α,β-dimethylcinnamic acid with hydrogen bromide and oxygen by Simamura, Nomura, and the present author[9], which has not yet been published, showed that it gives α-bromoacetophenone and acetophenone by the reaction with hydrogen bromide and oxygen.

Diphenylethylene gave a large amount of the dibromide and a very small amount of *p*-bromophenol by the reaction with bromine and oxygen. This result is apparently inconsistent with the result discussed above. It is to be noted, however, that diphenylethylene has no reactive hydrogen in the molecule, so that the peroxide radical produced from oxygen and bromo free radical (reaction 4′), cannot give a bromohydroperoxide. In the case of α,β-dimethylstilbene, it may be possible that the methyl groups serve as hydrogen donors for the bromo peroxide radical by either an inter- or an intramolecular mechanism. Although the electronic effect of the methyl groups attached to the carbon atoms of the ethylenic linkage on the reactivity with bromine and oxygen has not been discussed, the present author considers such an effect as mentioned above possible, but at present no experimental evidence for the effect is available.

M. S. Kharasch, A. Fono, and W. Nudenberg[10] reported that diphenylethylene gave phenol and acetophenone by the reaction with hydrogen peroxide in the presence of perchloric acid. The present author also observed a special reactivity of β-methylcinnamic acid with hydrogen peroxide in the presence of perchloric acid. β-Methylcinnamic acid was decomposed to give carbonyl compounds, while cinnamic acid did not give any product under the same conditions. Investigation on the reaction is continued.

Experimental

Materials.—β-Methylcinnamic acid was synthesized by the Reformatsky reaction of acetophenone with ethyl iodoacetate in benzene, and recrystallized from ethyl alcohol, m.p. 104.5°. α-Methylcinnamic acid was synthesized by the Perkin reaction of benzaldehyde with propionic anhydride in the presence of sodium propionate, and recrystallized from ethyl alcohol, m.p. 81~82°C. The preparation of *p*-methoxycinnamic acid, atropic acid, and diphenylethylene, and their purification were described in a previous paper[2].

The Reaction of β-Methylcinnamic acid with Bromine and Oxygen.—β-Methylcinnamic acid (2 g.) was dissolved in 60 ml. of benzene and the solution was divided into equal portions in separate flasks, each being equipped with a small dropping funnel, and one in addition with two glass tubes for introducing oxygen into the solution. The flasks were placed in the strong sunlight, and 20 ml. of a benzene solution containing 1 g. of bromine was dropped into each flask, oxygen being passed simultaneously into one of the solutions. Here the experiment with introduction of oxygen is designated as Expt. 42-a, and the experiment without oxygen as Expt. 42-b. The color of the solution in Expt. 42-b faded in less than five minutes, while that of Expt. 42-a slowly and remained even for four hours. No evolution of hydrogen bromide was observed during the reaction in either case. In Expt. 42-a, after oxygen was passed for about 130 minutes, the solution was kept standing in the diffused daylight for 210 minutes. From the reaction mixture, 0.31 g. of crystalline substance and 0.852 g. of an oil were obtained. The oil

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[9] O. Simamura, S. Nomura, and M. Takahasi, unpublished work.

[10] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(0.852 g.) was brought to react with 0.5 g. of 2,4-dinitrophenylhydrazine dissolved in 40 ml. of ethyl alcohol with 1 ml. of conc. hydrochloric acid, and about 0.239 g. of a 2,4-dinitrophenylhydrazone, m.p. 220~235°C, was obtained. The chloroform solution of the dinitrophenylhydrazone was passed through a chromatographic column of alumina, giving an orange zone and a dark brown zone. Acetophenone 2,4-dinitrophenylhydrazone, m.p. 248~250°C, was obtained from the latter zone, and identified by the mixed melting point. The orange zone gave a very small amount of an unidentified substance. The crystalline product (0.31 g.) was identified with the dibromide of β-methylcinnamic acid by the mixed melting point.

From Expt. 42-b, about 1.93 g. of β-methylcinnamic acid dibromide, m.p. 128°C, was obtained, but no oily product.

In another experiment similar to Expt. 42-a, 30 ml. of a benzene solution containing 1 g. of β-methylcinnamic acid was treated, in the sunlight for 320 minutes, with oxygen and with 30 ml. of a benzene solution containing 1 g. of bromine simultaneously. The gas from the solution was passed through distilled water and then through an aqueous barium hydroxide solution. The distilled water then gave a positive Schiff test, indicating the formation of a water-soluble aldehyde. When the benzene solution was washed with 10 ml. of distilled water, the aqueous layer gave positive reactions in Schiff test, with 2,4-dinitrophenylhydrazine, and with dimedone. An alcohol solution of dimedone gave a very small amount of a crystalline substance, m.p. 195~200°C, but its identification was unsuccessful. Barium carbonate precipitated from the aqueous barium hydroxide during the reaction weighed 0.707 g. (0.0031 mol.).

The Influence of Oxygen on the Reaction of Other Ethenoid Compounds with Bromine.—To a solution of 4 g. of cinnamic acid in 40 ml. of benzene, 30 ml. of a benzene solution containing 4.7 g. of bromine was added dropwise with passage of oxygen in the sunlight for 125 minutes. The color of bromine disappeared in about one hour. The gas from the solution was passed through distilled water and then through a barium hydroxide solution, but no barium carbonate was formed in the barium hydroxide solution, and neither the bromide ion nor a carbonyl compound was found in the distilled water. From the benzene solution about 5.9 g. of crystalline cinnamic acid dibromide precipitated, and on evaporation of the mother liquor 1 g. of slightly oil-stained crystals of cinnamic acid dibromide were further obtained.

p-Methoxycinnamic acid (1 g.) was dissolved in 60 ml. of carbon tetrachloride, and the solution was divided into two flasks. Into each flask 0.28 g. of bromine dissolved in 20 ml. of carbon tetrachloride was added in the sunlight, oxygen being passed into one of the solutions. The color of bromine faded nearly at the same rate in both solutions, and no remarkable inhibition by oxygen from addition of bromine to the ethenoid compound was observed. Hydrogen bromide was not evolved in the course of reaction, and it was suggested that addition of bromine to the double bond took place more predominantly than nuclear substitution.

The same experimental procedure as above was followed in the case of atropic acid and diphenylethylene. From atropic acid, only atropic acid dibromide, m.p. 115~116°C, was obtained either with or without introduction of oxygen. In the case of diphenylethylene, the reaction mixture was shaken with water and aqueous alkali successively. When a bromine potassium bromide solution was added to the neutral aqueous extract, tribromophenol was precipitated. Moreover, when the alkaline extract was saturated with carbon dioxide and extracted with ether, a very small amount of a phenolic substance was obtained, which showed a positive test of a phenol with ceric ammonium nitrate, and had a melting point, 63.5°C. Diphenylethylene dibromide was obtained from the both carbon tetrachloride solution on removing the solvent by distillation.

Reaction of β-Methylcinnamic Acid with Hydrogen Bromide and Oxygen.—β-Methylcinnamic acid (5.000 g.) was suspended in 70 ml. of carbon tetrachloride, and a mixture of hydrogen bromide and oxygen was passed through the suspension for 485 minutes. Here the treatment was continued longer than in the cases of the other ethenoid compounds, because preliminary experiments showed that the reaction was not completed in spite of a relatively long reaction time. A moderate amount of carbon dioxide was evolved during the whole reaction period, giving 0.608 g. of barium carbonate. About 1.5 g. of brown oil separated from the carbon tetrachloride solution. The carbon tetrachloride solution was shaken three times with 70 ml. of distilled water, and then twice with 30 ml. of 2 N aqueous sodium hydroxide. The sodium hydroxide solution was saturated with carbon dioxide, separating about 3 ml. of an oil, which was extracted with ether. Benzoyl chloride was added to 1 ml. of the oil, and the mixture was heated for some time, and poured into water. The crystalline product, after washed with aqueous sodium carbonate, was recrystallized from ethyl alcohol, giving a white crystalline substance, m.p. 102~104°C. It was identified with *p*-bromophenyl benzoate by the mixed melting point with an authentic specimen. *Anal.* Found: Br, 29.5. Calcd. for $C_{13}H_9O_2Br$: Br, 28.9%. The sodium hydroxide solution, from which the phenolic substance had been separated, was acidified with dil. sulfuric acid, and shaken twice with 100 ml. of ether. Evaporation of the ethereal solution gave about 0.321 g. of a pale yellow oil, which contained only a trace of bromine. It was presumably crude β-methylcinnamic acid, although it could not be brought to crystallization.

In another similar experiment, hydrogen bromide and oxygen were passed into a solution of β-methylcinnamic acid (10 g.) in 80 ml. of benzene for 360 minutes, and 2.2 g. of a precipitate was obtained which was identified with β-methylcinnamic acid dibromide. Evaporation of the benzene solution gave a yellow oil. When 1.1 g. of the oil was brought to reaction with 2,4-dinitrophenylhydrazine in ethyl alcohol, a small amount of a yellow precipitate was formed. It was separated into parts soluble and insoluble in hot ethyl alcohol. The soluble part was a yellow crystalline substance, which melted at 160~164°C. The insoluble part, which weighed 0.05 g., melted at 210°C, and contained 15.8% of bromine. Further purification was unsuccessful with both substances, but the soluble substance was supposed to be 2,4-dintrophenylhydrazone of formaldehyde or of glyoxylic acid, and the insoluble to be that of α-bromoacetophenone, m.p. 214~215°C.

When hydrogen bromide was passed through a solution of 3 g. of β-methylcinnamic acid in 60 ml. of benzene without introduction of oxygen for 210 minutes, a crystalline substance, m.p. 42~80°C, was obtained, but recrystallization gave β-methylcinnamic acid only.

A reaction of α-methylcinnamic acid with hydrogen bromide and oxygen was attempted in the same way as that of β-methylcinnamic acid. No evolution of carbon dioxide was observed, and the reaction mixture gave no positive tests of a carbonyl compound, and α-methylcinnamic acid was recovered from the solution.

The Reaction of Cinnamic Acid with Hydrogen Peroxide in the Presence of Perchloric Acid.—Cinnamic acid (6.0 g.) was dissolved in 40 ml. of acetic acid, and 6 ml. of 30% hydrogen peroxide and 2 g. of 70% perchloric acid were added. Even after two days, cinnamic acid was recovered almost completely, and no formation of either a carbonyl compound or a phenol was observed. A preliminary experiment on the reaction of β-methylcinnamic acid with hydrogen peroxide in the presence of perchloric acid has shown the formation of acetophenone and glyoxylic acid.

Ultraviolet Absorption Spectra of Cinnamic Acid and its Derivatives.—The measurements of the ultraviolet absorption spectra were carried out with a Beckman type spectrophotometer. The absorption maxima of cinnamic acid, β-methylcinnamic acid and β-ethylcinnamic acid in 94% ethyl alcohol, were 273, 260 and 244 mμ, respectively, and the molecular extinction coefficients were 2.2×10^4, 1.5×10^4 and 1.0×10^4, respectively.

Summary

The action of oxygen and bromine on β-methylcinnamic acid in benzene in the sunlight at room temperature caused an oxidative cleavage of the double bond, giving acetophenone and carbon dioxide, in addition to β-methylcinnamic acid dibromide. Similar experiments with cinnamic acid, atropic acid, *p*-methoxycinnamic acid, gave only dibromides either with or without introduction of oxygen.

Although a complete identification of the reaction products from the reaction of hydrogen bromide and oxygen on β-methylcinnamic acid was unsuccessful, it was found that a phenolic substance and a carbonyl compound were produced and that the formation of the phenol inhibited the progress of the reaction.

On the ground of these and other results which were described in the three preceding papers, the mechanism of the reactions of hydrogen bromide, bromine, and oxygen with ethenoid compounds is discussed.

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