# The Addition of Hydrogen Bromide to Crotonic Acid in Carbon Tetrachloride Solution and the Oxygen Effect.

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Recent investigations on the addition of hydrogen halides to ethenoid compounds have centred in the abnormal addition of hydrogen bromide, in which oxygen, organic peroxides, and ferromagnetic metals such as reduced nickel and iron reverse the direction of addition which should otherwise follow the Markownikoff rule. The works in this field have been reviewed by J. C. Smith(1) from one point of view and by F. R. Mayo and C. Walling(2) from another. The view(3) developed in this laboratory concerning the oxygen effect on hydrogen bromide reacting with ethenoid compounds is supported by a series of the experimental facts which have been obtained with a variety of substances(4). It has been established that a bromine atom delivered from hydrogen bromide by the action of oxygen in the presence of an ethenoid compound causes an abnormal addition by a chain mechanism, attaching itself to the double bond of the ethenoid compound to yield a free bromo radical, which reacts then with hydrogen bromide to give the final product of the addition reaction with regeneration of another bromine atom. In many cases of the abnormal addition the bromine atom is oriented to the carbon atom which would take up hydrogen in the normal addition, thus giving rise to the formation of an abnormal product different from the normal one. There are, however, no theoretical grounds to expect that such will be the case in all ethenoid compounds.

The nature of the substitution at the double bond is no doubt a factor to determine the direction of addition. Although the mechanism of the normal addition is still in controversy, if it is assumed that hydrogen halides behave as polar molecules when they add to olefins, the direction of addition will depend on the polarity of the double bond. According to Smith(5), R. Robinson suggested that the direction of addition of hydrogen bromide to olefins could be predicted from a knowledge of the directive powers of the relevant groups when attached to the benzene nucleus: As the ortho and para directing groups not conjugated with the benzene nucleus all force electrons towards the nucleus, they should do so in compounds of the type $CH_2 = CHX$, where consequently the normal product should be $CH_3CHBrX$, which agrees with the Markownikoff rule. With meta directing groups the reverse should be the case.

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(1) J. C. Smith, *Chem. and Ind.*, **56** (1937), 833; **57** (1938), 461; *Ann. Reports*, **36** (1940), 219.

(2) F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

(3) Y. Urushibara, *J. Chem. Soc. Japan*, **60** (1939), 717.
Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323.

(4) O. Simamura, *ibid.*, **15** (1940), 292.

(5) J. C. Smith, *Chem. and Ind.*, **57** (1938), 461.

This hypothesis seems to have been substantiated by a great number of experimental facts. However, M. S. Kharasch, E. H. Rossin and E. K. Fields(6) recently obtained 1,1,1,2-tetrachloropropane by adding hydrogen chloride to trichloromethylethylene, although they could not add hydrogen bromide under antioxidant conditions. This result agrees with the Markownikoff rule, but is not in accordance with what is predicted from Robinson's hypothesis, trichloromethyl being considered a meta directing group(7).

The orientation of the bromine atom in the abnormal addition is a different matter, perhaps more complex. It may reasonably be assumed that a free bromine atom is directed towards the carbon atom with the higher electron density(8). Thus, for example, in allyl bromide, which is considered to be polarised as indicated below, in the symbols of the English school,

$$\overset{\curvearrowleft}{\mathrm{CH_2{=}}}\mathrm{CH} \leftarrow \mathrm{CH_2Br}\,,$$

a bromine atom is directed towards the $\gamma$ carbon atom to yield finally 1,3-dibromopropane, the abnormal product. The hypothesis is the more attractive in so far as it brings, in conjunction with the polarisation of the double bond as postulated by Robinson, the orientation of the hydrogen bromide in the normal addition and the reversal of it in the abnormal addition into a consistent correlation. That the hypothesis of the greater reactivity of the carbon atom with the higher electron density may sometimes fail is shown by the instance of trichloromethylethylene cited above. As the trichloromethyl group is meta directing when attached to the benzene nucleus, it attracts electrons to itself; therefore, according to the hypothesis the product should be 1,1,1-trichloro-2-bromopropane when the mechanism involving bromine atoms is in operation, whereas 1,1,1-trichloro-3-bromopropane was really obtained under oxidant conditions.(6)

Another view is suggested by F. R. Mayo and C. Walling(2) with additional advantages. The point of attack by the bromine atom is little affected by the polarity of double bond, but depends upon the relative stability of the two bromo radicals which may be formed. To exemplify the theory, allyl bromide gives 1,3-dibromopropane in the abnormal addition because the order of the stabilities is as follows,

$$\mathrm{CH_2Br{-}\underset{|}{C}H{-}CH_2Br} > \mathrm{\underset{|}{C}H_2{-}CHBr{-}CH_2Br}\,.$$

However, why the former radical is more stable than the latter remains to be explained. Perhaps the idea of hyperconjugation(9), i.e., conjuga-

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(6) M. S. Kharasch, E. H. Rossin and E. K. Fields, *J. Am. Chem. Soc.*, **63** (1941), 2558.

(7) A. F. Holleman, J. Vermeulen and J. de DeMooy, *Rec. trav. chim.*, **33** (1914), 1. K. Lauer, *J. prakt. Chem.*, **142** (1935), 252.

(8) M. S. Kharasch, H. Engelmann and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 288.

(9) See, for example, R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Am. Chem. Soc.*, **63** (1941), 41.

tion with saturated groups, would account for the assumed order of decreasing stabilities of aliphatic free radicals, tertiary>secondary> primary. In the tertiary radical the free valency electron can conjugate with three groups, while in the secondary one it can do so with two groups at most, thus the former being more stable by the energy acquired through the extra conjugation with the third additional group. From the same argument it is concluded that the secondary radical is more stable than the primary one.

The hypothesis of the radical stability could most satisfactorily explain the observations with crotonic acid⁽¹⁰⁾ which gives always β-bromobutyric acid irrespective of the conditions of addition, because the β-bromo radical $CH_3CHBr\underset{|}{C}HCOOH$ should be more stable than the α-isomeride, $CH_3\underset{|}{C}HCHBrCOOH$, by virtue of the conjugation of the free valency electron with the carboxyl group. The formation of β-bromobutyric acid as a normal product is in accord with the prediction from Robinson's hypothesis.

Propenylbenzene⁽¹¹⁾ and cinnamic acid⁽¹²⁾ are stated to give with hydrogen bromide always 1-phenyl-1-bromopropane and β-bromohydrocinnamic acid, respectively. Although a discussion of these findings seems to be rather hasty as the full experimental details are not available, they may be considered to indicate on the basis of the theory of the radical stability that the radicals $C_6H_5CHBr\underset{|}{C}HCH_3$ and $C_6H_5CHBr\underset{|}{C}HCOOH$ should be more stable than $C_6H_5\underset{|}{C}HCHBrCH_3$ and $C_6H_5\underset{|}{C}HCH_2COOH$, respectively. This is unexpected because theoretically the latter radicals should be more stable as the conjugation of the free valency electrons with phenyl groups would contribute much more to the stabilisation of the free radicals. Attention must be paid to another factor determing the orientation of hydrogen bromide in the abnormal addition. It concerns the reaction between the free bromo radical and hydrogen bromide where the final addition product and a bromine atom are yielded. When a free radical stabilised by the conjugation of the free valency electron with some groups reacts with hydrogen bromide, it would require a greater activation energy and consequently would react slower than when such stabilisation is absent. Then the reactivity of the free bromo radicals may be a predominant factor to determine the direction of addition of hydrogen bromide. Thus, those olefins with a phenyl group in conjugation with double bond may give results apparently contradictory to the theory of radical stability.

At this stage of development, where the problem of the orientation of hydrogen bromide has not reached a complete solution, accumulation of more experimental data is desirable.

Addition of hydrogen bromide to crotonic acid has already been studied⁽¹⁰⁾ with results that β-bromobutyric acid is the only product obtainable irrespective of the conditions of addition and there seems to

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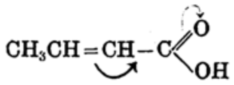
(10) C. Walling, M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 2693. D. C. Grimshaw, J. B. Guy and J. C. Smith, *J. Chem. Soc.*, **1940**, 68.

(11) Unpublished work of M. S. Kharasch, P. C. White and F. R. Mayo cited by F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

(12) A. Michael and G. H. Shadinger, *J. Org. Chem.*, **4** (1939), 128.

be no indication of the accelerated reaction under oxidant conditions. Walling, Kharasch, and Mayo suggested that the chain mechanism might not operate when the double bond is conjugated with a carboxyl group, but they did not exclude the possibility that both mechanisms, normal and abnormal, yield the identical product. Smith and co-workers(10) are of the opinion that bromine is not attracted to the $\alpha$-carbon atom of crotonic acid since there is no accumulation of electrons in that position, the mesomeric polarisation in the molecule being such as represented by the formula.



$$CH_3CH=CH-C\begin{array}{l}/\!\!/O\\ \backslash OH\end{array}$$

As the action of the mixture of hydrogen bromide and oxygen on allyl bromide and certain other ethenoid compounds has proved to be a very useful method for elucidating the mechanism of the abnormal addition(3)(4), the same method has now been applied to crotonic acid to determine whether a similar chain mechanism operates when hydrogen bromide is added to this acid under oxidant conditions.

Into a suspension of 10 g. of crotonic acid in 50 c.c. of carbon tetrachloride the mixture of hydrogen bromide and oxygen was passed in the dark. The reaction vessel was cooled with ice water throughout the passage of the gas mixture. At the end of three hours the reaction mixture was found to have deposited a few c.c. of a pale brown oil, which on treatment as described in the experimental part yielded $\alpha$-hydroxy-$\beta$-bromobutyric acid, m.p. 97–98°C. The carbon tetrachloride layer was colourless and on removal of the solvent 17 g. of an oil was obtained. It was distilled under diminished pressure and the first fraction, which passed over at 122–127° at 18 mm., was redistilled to yield 4.85 g. of $\beta$-bromobutyric acid, b.p. 94–98° at 4 mm., $n_D^{20}$ 1.4782. When this was solidified by cooling with ice and then gradually warmed, the last pieces of crystals disappeared at 14°. If any $\alpha$-bromobutyric acid was formed, it would be present in the head fraction as it boils lower than the $\beta$-isomeride, and as this fraction melted at 14°, whereas the $\alpha$-bromo-acid melts at $-4°$(13), it seems to have contained no appreciable amount of the $\alpha$-isomeride. In the first distillation, as the temperature of the bath was raised, the thermometer reading rose continually from 127° and, when it reached 148°, the distillation was stopped as the distilling liquid solidified to a crystalline mass filling the arm of the distilling flask. The crystals were identified as crotonic acid dibromide, m.p. 86–88°. The residue in the flask also solidified on cooling to crystals of the same substance embedded in viscous oil. Thus the reaction products remaining in carbon tetrachloride were found to consist mainly of $\beta$-bromobutyric acid and crotonic acid dibromide. That $\alpha$-bromobutyric acid was not detected is in accord with the findings of the foreign workers(10). The formation of some substances of peroxidic nature is certain, although they were not identified, as the carbon tetrachloride solution and the brown oil liberated iodine from aqueous potassium iodide, while any of the three compounds isolated was found not to do so even when acidified with hydrochloric acid. Fur-

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(13) Lespieau, *Compt. rend.*, **139** (1904), 739.

ther, crotonic acid dissolved in carbon tetrachloride and placed in diffuse light for a day developed no coloration with ferrous ammonium sulphate and ammonium thiocyanate. Thus it is concluded that reactions of the same type occurred as when the gas mixture was allowed to react with allyl bromide⁽³⁾. The formation of crotonic acid dibromide is a convincing evidence in support of the view that the reaction involved bromine atoms, which, in reacting with crotonic acid, must have attacked the β-carbon atom, as no α-bromobutyric acid or its derivatives were detected.

Isolation of α-hydroxy-β-bromobutyric acid was unexpected. If hydrogen peroxide or an organic peroxide formed⁽³⁾ in the course of the reaction should yield with crotonic acid α, β-epoxybutyric acid, this would readily react with hydrogen bromide to give the hydroxybromobutyric acid as described in the experimental part. However, the observed formation of the hydroxybromobutyric acid may be adduced in substantiation of the view that the reaction involved the formation of the bromine atom and that the bromine atom attached itself to the β-carbon atom of crotonic acid. Then the formation of the hydroxybromo-acid is interpreted as follows: In the first place a β-bromo radical acid is formed by the combined action of hydrogen bromide and oxygen or by the action of a bromine atom on crotonic acid

$$2CH_3CH{=}CHCOOH+2HBr+O_2 \longrightarrow 2CH_3CHBr\underset{|}{C}HCOOH+H_2O_2$$

$$CH_3CH{=}CHCOOH+Br \longrightarrow CH_3CHBr\underset{|}{C}HCOOH\ .$$

This radical acid then reacts with oxygen or hydrogen peroxide formed to yield finally the acid under consideration.

Oxygen having been shown to cause the reaction involving bromine atoms, it was expected that it might more or less accelerate the addition reaction, and its effect on the rate was examined. Hydrogen bromide (0.0135 mole) was allowed to react with crotonic acid (0.0128 mole) in carbon tetrachloride (10 c.c.) in a glass tube with a capacity of 60 c.c. for three hours in the dark at room temperature either in presence or in absence of oxygen. From the reaction mixture carbon tetrachloride and the unreacted hydrogen bromide were removed under reduced pressure and the remaining oil was treated with a sodium hydroxide solution and analysed for liberated bromide ion. The extent of reaction of crotonic acid was calculated on the assumption that the liberated bromide ion gives the amount of β-bromobutyric acid formed and no other products were yielded at all. It is obvious from the results tabulated below, that, contrary to the expectation, oxygen did not exert any perceptible influence on the rate of the reaction when the amount of oxygen admitted was small. The extent of addition decreased slightly as the amount of oxygen was increased. That in these cases the side reaction involving oxygen as has been described above took place appreciably was demonstrated by the turbid appearrance of the reaction mixture when the greater part of the solvent was removed. No acceleration by oxygen of the addition of hydrogen bromide to crotonic acid might be taken to indicate that the bromo radical acid reacts readily with oxygen but not with hydrogen bromide to continue the chain reaction, which would superpose itself on the rapid normal addition. There is indeed an incipient formation of chains by the joint action of hydrogen bromide and oxygen but they cannot develop to a noticeable abnormal addition reaction.

Table.

The Addition of Hydrogen Bromide to Crotonic Acid in the Presence of Oxygen in Carbon Tetrachloride Solution in the Dark.

| Experiment Series | Experiment No. | Oxygen admitted mm. Hg | Crotonic acid reacted % | Temp. | Method of analysis* |
|---|---|---|---|---|---|
| I | 1 | 0 | 66.9 | 19–20 | a |
| | 2 | 0 | 66.5 | | a |
| | 3 | 36† | 68.5 | | a, b |
| II | 4 | 0 | 68.0 | 20 | b |
| | 5 | 47 | 68.2 | | b |
| | 6 | 63 | 68.1 | | b |
| III | 7 | 0 | 69.8 | 20 | b |
| | 8 | 157 | 66.7 | | b |
| | 9 | 274 | 62.5 | | b |

Crononic acid, 0.0128 mole; hydrogen bromide, 0.0135 mole; carbon tetrachloride, 10.0 c.c. Reaction time, three hours. Experiments belonging to the same series were conducted in quick succession.

* As regards the methods of analysis adopted see the experimental part.

† The amount of oxygen is 0.092 millimole.

## Experimental Part.

**Materials.** Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a bottle containing cold tertalin and then through a tube filled with anthracene. It was dried by passage through a tube filled with glass wool sprinkled with phosphorus pentoxide and was conducted into a reaction vessel after mixing with oxygen which was taken from a cylinder and dried with phosphorus pentoxide. When the effect of oxygen on the extent of addition was investigated, the hydrogen bromide dried with phosphorus pentoxide was collected in a tube cooled with liquid air. It was melted, solidified again, and the tube was evacuated with a mercury diffusion pump. The process was repeated three times and the hydrogen bromide was fractionated, the middle portion being used. Crotonic acid was recrystallised from petroleum ether and the purified sample melted at 72–73°. Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and fractionated after desiccation with phosphorus pentoxide.

**The Action of the Mixture of Hydrogen Bromide Gas and Oxygen on Crotonic Acid in Carbon Tetrachloride in the Dark.** The essential part of the experiment has already been described above. The pale brown oil which was deposited from the reaction mixture weighed 4.2 g. and, when a little water was added, complete solution took place. This was extracted with ether and the ethereal solution was dried with anhydrous sodium sulphate. On removing the ether under reduced pressure hexagonal plates insoluble in carbon bisulphide and very soluble in cold water were obtained. The product crystallized from water was dissolved in ether and by adding a little petroleum ether crystals melting at 97–98° were obtained; yield, 0.5 g. (Found: Br, 43.8. Calculated for $C_4H_7O_3Br$: Br, 43.6%). Its properties coincide with those described for α-hydroxy-β-bromobutyric acid. According to P. Melikoff⁽¹⁴⁾, when the sodium salt of α-hydroxy-β-halocarboxylic acid is boiled in aqueous solution, carbon dioxide splits off and aldehyde or ketone results according to the constitution of the original acid. The substance obtained here was dissolved in a dilute sodium carbonate solution and heated, when the characteristic odour resembling that of acetaldehyde evolved. Although it was not characterized by the formations of derivatives, there is no doubt that propionaldehyde was formed. The melting point of the substance was not depressed on admixture with an authentic specimen of α-hydroxy-β-bromobutyric acid prepared by the action of hydrogen bromide on α, β-epoxybutyric acid (methylglycidic acid).

**α-Hydroxy-β-bromobutyric Acid from Methylglycidic Acid.** Methylglycidic acid (0.3 g.) prepared from α-bromo-β-hydroxybutyric acid following the direction given by Melikoff(15) for α-chloro-β-hydroxybutyric acid was suspended in 25 c.c. of carbon tetrachloride and the mixture of hydrogen bromide and oxygen(16) was passed for an hour and a half. The acid changed into a sticky mass. The carbon tetrachloride was decanted and the product was crystallized from water, m.p. 96–98°.

**The Effect of Oxygen on the Addition of Hydrogen Bromide to Crotonic Acid in Carbon Tetrachloride in the Dark.** In a glass tube with a capacity of 60 c.c. 1.1 g. of crotonic acid and 10 c.c. of carbon tetrachloride were placed and the tube was connected to the vacuum line. To remove the oxygen the contents of the tube were solidified by cooling with liquid air and the tube was evacuated with a mercury diffusion pump. The contents were then melted, again solidified, and the tube evacuated. The procedure was repeated three times. Then 0.0135 mole of hydrogen bromide (0.5 c.c. of liquefied hydrogen bromide at the temperature of solid carbon dioxide) was condensed on the top of the solidified mixture and oxygen was introduced to a specified pressure. The tube was sealed off and shaken manually as uniformly as possible. After three hours the capillary tip of the reaction tube was connected to a pump by means of a piece of rubber tubing, the tip was broken by crushing it from outside and the remaining hydrogen bromide and the greater part of carbon tetrachloride were removed. The remaining oily product was transferred to a 50 c.c. Erlenmeyer flask, which was then placed in a desiccator containing potassium hydroxide and scraps of paraffin. The desiccator was evacuated for three hours and left overnight. The product (0.2–0.3 g.) was treated with 5 c.c. of 1N sodium hydroxide solution, heated for thirty minutes on a water-bath, and by adding silver nitrate to the solution acidified with dilute nitric acid silver bromide was precipitated and weighed. This method of analysis is referred to as (a) in the accompanying table. Another method (b) consisted in heating the sample with 5 c.c. of 1N sodium hydroxide solution for five minutes and titrating the liberated bromide ion by the Volhard method. Both methods were found to give the identical value when applied to the product of Exp. No. 3.

## Summary.

(1) Hypotheses suggested to explain the orientation of hydrogen bromide in the addition to the ethenoid compound have been briefly reviewed and critisized.

(2) Allowing the mixture of hydrogen bromide and oxygen to react with crotonic acid in carbon tetrachloride, three products, β-bromobutyric

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(14) P. Melikoff and Petrenko-Kritschenko, *Ann.*, **266** (1891), 370; *Chem. Zentr.*, **1890**, I, 524.

(15) P. Melikoff, *Ber.*, **16** (1883), 1270.

(16) For the preparation oxygen is not necessary.

acid, crotonic acid dibromide and α-hydroxy-β-bromobutyric acid, have been isolated.

(3) Oxygen has been found not to accelerate the addition of hydrogen bromide to crotonic acid in carbon tetrachloride solution in the dark.

(4) It is concluded that in the addition of hydrogen bromide to crotonic acid in the presence of oxygen, this participates in the reaction producing free bromo-radical acid and bromine atoms, the latter being attached to the β-carbon atom of crotonic acid, but that the chains involving these cannot develop because of the ready reaction of the bromo radical acid with oxygen rather than with hydrogen bromide.

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