The Addition of Hydrogen Bromide to Cinnamic Acid and the Oxygen Effect.(1)

By Osamu SIMAMURA and Makoto TAKAHASI.

(Received November 16, 1948.)

The problem of the oxygen effect in the addition of hydrogen bromide to ethylenic compounds, manifesting itself in the reversal of the direction of addition expected from Markownikoff's rule, appears to have been settled so far as its general character is concerned.(2) The active agents which cause the abnormal addition have turned out to be bromine atoms produced from hydrogen bromide under relevant experimental conditions.

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(1) Presented at the 68th Annual Meeting of the Chemical Society of Japan in Tokyo, October 18, 1946.

(2) For reviews of the subject see Y. Urushibara, *Kwagakusoho*, **6** (1944), 185; F. R. Mayo and C. Walling, *Chem. Rev.*, **27** (1940), 351.

A bromine atom adds to the ethylenic bond to produce a free radical containing bromine, and this reacts with hydrogen bromide yielding a molecule of the final addition product and another bromine atom, the latter in turn attaching itself to another molecule of the ethylenic compound to reproduce the free radical:

$$\mathrm{RCH=CHR'+\dot{B}r \rightarrow RCHBr\dot{C}HR'},$$
$$\mathrm{RCHBr\dot{C}HR'+HBr \rightarrow RCHBrCH_2R'+\dot{B}r}.$$

Thus a chain reaction occurs, and in each cycle one molecule of the abnormal addition product is produced. However, concerning essential factors deciding the position of attack by the bromine atom and hence the orientation of hydrogen bromide a consensus of opinion has not yet been attained. Furthermore, in such cases as crotonic(3,4,5) and cinnamic(4) acids no reversal has ever been observed, the products under the oxygenic or peroxidic condition being identical with those under the normal condition, and with regard to the mechanism of the phenomena several theories have been set forth by various workers.

The investigation on the addition of hydrogen bromide to crotonic acid reported from this Laboratory(5) was a contribution to elucidation of these moot questions. A small amount of oxygen was found not to influence the addition of hydrogen bromide to crotonic acid either in the direction of addition, β-bromobutyric acid being the sole product, or in the rate of the reaction. The mixture of hydrogen bromide and oxygen, however, reacted with crotonic acid in carbon tetrachloride giving rise to three products, β-bromobutyric acid, crotonic acid dibromide, and α-hydroxy-β-bromobutyric acid. It was therefore concluded that, in the addition of hydrogen bromide to crotonic acid in the presence of oxygen, the oxygen participates in the reaction, as is the case with ordinary ethylenic compounds, producing bromine atoms from hydrogen bromide, and then the bromine atoms attach themselves to the β-carbon atom of crotonic acid to yield a free radical, $\mathrm{CH_3CHBr\dot{C}HCOOH}$. The bromo radical gives rise to α-hydroxy-β-bromobutyric acid by a ready reaction, in contrast to radicals from the common ethylenic compounds, with oxygen rather than with hydrogen bromide. If the free radical had abstracted a hydrogen atom from a molecule of hydrogen bromide to yield β-bromobutyric acid and a bromine atom, the usual chain reaction of the abnormal addition would have taken place, and the addition to crotonic acid would have proceeded more rapidly in the presence of oxygen than in its absence. The experimental identification of the β-carbon atom of crotonic acid as the site of attack by bromine atoms supports the theory suggested by Mayo and Walling(2) that of the alternative free radicals which can be produced by addition of a bromine atom the more stable is the one to be preferentially

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

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

(5) O. Simamura, this Bulletin, **17** (1942), 326.

produced. For the free radical $CH_3CHBr\dot{C}HCOOH$ is considered more stable than the isomeric radical $CH_3\dot{C}HCHBrCOOH$ by the resonance energy due to the conjugation of the odd electron at the α-carbon atom with the carboxyl group, whereas such an effect is absent in the later radical.

Experiments have now been extended to cinnamic acid. According to A. Michael(4) cinnamic acid added hydrogen bromide to give only β-bromohydrocinnamic acid, but the result does not appear to be conclusive, as it does not seem that, in his investigation, due attention was paid to the various factors now accepted as influencing the course of the addition reaction.

Cinnamic acid was subjected to the action of hydrogen bromide in the presence of either benzoyl peroxide or catechol in benzene in a sealed tube kept at 60°C. The product in either case was found to be β-bromohydrocinnamic acid, and no appreciable difference in the reaction velocity was observed. On the other hand, when a mixture of hydrogen bromide and oxygen was passed into a suspension of cinnamic acid (10 g.) in benzene (70–80 c.c.) in the dark for 4 to 7 hours, the reaction vessel being cooled with ice water, a rather vigorous reaction took place with the evolution of heat. In the course of the reaction, water and a deposit, identified as α,β-dibromohydrocinnamic acid (m.p. 192°) as described in the experimental part, separated from the reaction mixture. On evaporation of the filtered benzene solution under reduced pressure at room temperature a residue was obtained, from which α,β-dibromohydrocinnamic acid and ω-bromoacetophenone were isolated. The ω-bromoacetophenone was certainly a scission product formed in the course of the reaction, and the other fragment, carbon dioxide, was found in the gas mixture escaping from the reaction vessel.

From these observations it is quite obvious that hydrogen bromide, oxygen, and cinnamic acid undergo a complicated reaction of just the same type as was already reported from this Laboratory.(6) Thus the course of the reaction is considered to be as follows: The simultaneous action of hydrogen bromide and oxygen on cinnamic acid produces a free radical $C_6H_5\dot{C}HCHBrCOOH$ and an unidentified substance (or substances) of peroxidic nature. α, β-Dibromohydrocinnamic acid is produced by the action of bromine liberated from hydrogen bromide by the action of the peroxidic substance on the free radical $C_6H_5\dot{C}HCHBrCOOH$,(7) a bromine atom being set free to add to cinnamic acid regenerating the same free

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(6) Y. Urushibara and O. Simamura, this Bulletin, **14** (1939), 323; O. Simamura, *ibid.*, **15** (1940), 292 and reference 5.

(7) In an investigation of the addition of bromine to cinnamic acid in carbon tetrachloride, one of the present authors (O. Simamura, this Bulletin, **17** (1942), 280) has postulated that the addition takes place through a chain mechanism involving bromine atoms and the free radical which is formed by attachment of a bromine atom to the double bond of cinnamic acid. The structure of the radical was tentatively assumed to be $C_6H_5CHBr\dot{C}HCOOH$ on the basis of evidences available at that time. From the present results it is now concluded that, in that case also, the radical must have the structure $C_6H_5\dot{C}HCHBrCOOH$.

radical. The acid may also be formed by the combined action of hydrogen bromide and oxygen on the free radical. The free radical is so stable that it cannot abstract a hydrogen atom from a molecule of hydrogen bromide to form α-bromohydrocinnamic acid and a bromine atom, which is subsequently to add to cinnamic acid forming the free radical and thus initiating the cyclic process of the chain addition reaction, but the free radical reacts at the β-carbon atom with oxygen, which has more or less unsaturated nature and is present comparatively in abundance in the reacting milieu, and ω-bromoacetophenone eventually is formed after decarboxylation.

There was no evidence to show the formation of the radical $C_6H_5CHBr\dot{C}HCOOH$, no compounds carrying a bromine atom on the carbon adjacent to the phenyl group, excepting α,β-dibromohydrocinnamic acid, having been obtained as reaction products. The isolation of α,β-dibromohydrocinnamic acid, which might be supposed to have been produced from the above radical and bromine, cannot be adduced as evidence in support of the formation of the radical in question, because, in view of the reactivity of such intermediate radicals in general, there is no reason why this radical should not react with oxygen as well, if not with hydrogen bromide, giving rise to products carrying a bromine atom on the carbon adjacent to the phenyl group.

The formation of the radical $C_6H_5\dot{C}HCHBrCOOH$ in preference to the alternative radical $C_6H_5CHBr\dot{C}HCOOH$ is easily accounted for on the basis of considerations analogous to those advanced by Mayo and Walling by the reasonable assumption that the former will be more stable than the latter because of the greater resonance energy due to the conjugation of the free valency electron on the β-carbon atom with the phenyl group than that due to the conjugation of the free valency electron on the α-carbon atom with the carboxyl group.

It was argued previously⁽⁵⁾ that if cinnamic acid was to add hydrogen bromide to give only β-bromohydrocinnamic acid even under the conditions favourable to the abnormal addition, this might well be attributable to the circumstances that the theoretically more stable radical $C_6H_5\dot{C}H$-$CHBrCOOH$, owing to its relatively great stability, reacts with hydrogen bromide with more difficulty than does the isomeric β-bromo radical. However, the possibility of the formation of β-bromohydrocinnamic acid through the chain mechanism under usual oxygenic conditions can now be ruled out, for, in the first place, the reaction under such conditions did not appear to be faster than that in the presence of catechol, and secondly, in the reaction with a large amount of oxygen it was demonstrated that only the α-carbon atom of cinnamic acid is attacked by bromine atoms.

β-Bromohydrocinnamic acid is formed only by the normal addition of hydrogen bromide, and that even in the presence of benzoyl peroxide. As the normal reaction is a slow one, it could not compete to advantage with the abnormal addition which should produce α-bromohydrocinnamic acid through the chain mechanism, if the radical $C_6H_5\dot{C}HCHBrCOOH$ were active enough to react readily with hydrogen bromide to initiate the chain.

In view of the relative stability of the radical postulated above it is supposed that the dimerization of it may have taken place. Although no compound resulting from the dimerization was found, this will not detract from the possibility of the operation of the reaction mechanism involving the free radical, inasmuch as the dimerization of usually scarce radicals would take place only under exceptionally favourable conditions provided by a very inert medium containing no reactive substances, such as oxygen.

Experimental Part

Materials. Hydrogen bromide was generated by dropping bromine on hot tetralin, and passed through a bottle containing cold tetralin, and then through a tube containing glass wool sprinkled with phosphorus pentoxide. For experiments in sealed tubes the hydrogen bromide was collected in a tube cooled with liquid air. Then the condensed hydrogen bromide was subjected to repeated fusion and solidification in vacuum to eliminate traces of incondensable gases. Cinnamic acid was synthesized from benzaldehyde, acetic anhydride, and anhydrous sodium acetate, and recrystallized from alcohol several times. It melted at 132.0–2.5°C. Carbon tetrachloride was refluxed with an alkaline permanganate solution, dried with anhydrous calcium chloride, and distilled. Benzene was shaken with concentrated sulphuric acid several times until the sulphuric acid layer was colourless, dried with calcium chloride, and distilled over sodium.

The Addition of Hydrogen Bromide to Cinnamic Acid in Benzene in a Sealed Tube. In a glass tube with a capacity of 70 c.c. cinnamic acid (4 g.) and benzene (15 c.c.) together with benzoyl peroxide (0.2 g.) or catechol (0.1 g.) were placed, and the tube was connected to the vacuum line. In order to remove 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 was evacuated to 0.0005 mm. of mercury. The procedure was repeated three times. Then a measured quantity of hydrogen bromide (1.5 c.c. at the temperature of solid carbon dioxide and ether) was condensed on the top of the solidified mixture, and the tube was sealed off. The tube was kept at about 60° in a hot water bath in the day-time. After five days the reaction tube was opened, and the benzene solution was filtered from a precipitate. The solid product (m.p. 134°, 4.9 g. in the experiment with catechol) which was already nearly pure was recrystallized from carbon disulphide and identified as β-bromohydrocinnamic acid. In the experiment with benzoyl peroxide, in addition to the above product (4.1 g.), on evaporation of the filtered benzene solution a solid residue (1.2 g., m.p. 98–123°) was obtained, from which a further crop of β-bromohydrocinnamic acid was separated.

The Action of the Mixture of Hydrogen Bromide and Oxygen on Cinnamic Acid in the Dark. The essential part of the experiments has already been described above. After the reaction was complete, the deposit (α, β-dibromohydrocinnamic acid, m.p. 192°) was separated from the solution, weighed (10.4 to 11.4 g.) and analyzed for bromine (found: Br, 48.2%). On recrystallization from carbon disulphide the bromine content was improved to 51.2% (calculated for $C_9H_8O_2Br_2$: Br, 51.9%). By removing the solvent from the solution under diminished pressure a residue (2.8 to 3 g.) consisting of a yellow oil and a small amount of a crystalline substance identified as α,β-dibromohydrocinnamic acid were obtained. The oil was dissolved in ether, dried with anhydrous sodium sulphate, and distilled under reduced pressure. The lachrymatory distillate, which passed over at 78–82° under 0.75 mm., was analyzed for bromine (found: Br, 39.2%). By cooling this distillate in an ice-box plate crystals were obtained, which after recrystallization from alcohol melted at 50–51° (found: Br, 40.2%; calculated for C_8H_7OBr: Br, 40.2%). The melting point of the substance was not depressed on admixture with an authentic specimen of ω-bromoacetophenone.

The gas issuing from the reaction vessel was passed through a bottle containing water and then through one containing an aqueous barium hydroxide solution. The precipitated barium carbonate was dried and weighed. The amount of carbon dioxide evolved was estimated at 0.089 to 0.209 mole per mole of the cinnamic acid used.

The product of addition of hydrogen bromide to cinnamic acid is β-bromohydrocinnamic acid either under the antioxidant condition or in the presence of benzoyl peroxide.

Summary

The action of the mixture of hydrogen bromide and oxygen on cinnamic acid in carbon tetrachloride produces ω-bromoacetophenone together with α,β-dibromohydrocinnamic acid. It is concluded that the free radical $C_6H_5\dot{C}HCHBrCOOH$ is formed in the intermediate stage in accord with the expectation from theoretical considerations concerning the stability of radicals. The radical, owing to its stability, does not react with hydrogen bromide to give α-bromohydrocinnamic acid, but reacts, on one hand, with oxygen ultimately to give ω-bromoacetophenone after disrupture of carbon dioxide and, on the other hand, with bromine or hydrogen bromide, as detailed in the text, to give α, β-dibromohydrocinnamic acid.

The authors express their sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work.

Chemical Institute, Faculty of Science,
University of Tokyo.