The Isomerization of Dimethyl Maleate by Hydrogen Bromide and by Hydrogen Chloride.

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Introduction. In the previous papers(1)(2) it was reported that hydrogen bromide, in presence of oxygen, caused the isomerization of isostilbene to stilbene in the dark at room temperature either in absence of solvents or in benzene solution, while neither hydrogen bromide nor oxygen was active when present alone. Reduced nickel, which is in itself inactive to the isomerization of isostilbene to stilbene, was found also to co-operate with hydrogen bromide to accelerate the isomerization in absence of solvents, and another ferromagnetic metal, reduced iron, was shown to be capable of promoting the isomerization with hydrogen bromide, although the effect was smaller than that of reduced nickel.

It may be added here that subsequent experiments have shown that no isomerization of isostilbene to stilbene takes place with hydrogen

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(1) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507.
(2) Y. Urushibara and O. Simamura, *ibid.*, **13** (1938), 566.

chloride either alone or in presence of any of oxygen, reduced nickel, and benzoyl peroxide under essentially the same experimental conditions as described in the cited reports.(1)(2)

The investigation has now been extended to the catalyzed isomerization of dimethyl maleate to dimethyl fumarate with the view of ascertaining whether oxygen co-operates with hydrogen bromide in accelerating the rearrangement just as that of isostilbene to stilbene, and it is the more interesting in view of the well-known conversion of maleic into fumaric acid by aqueous hydrogen halides,(3) which was investigated without taking account of the then unrevealed influence of oxygen. N. W. Hanson and D. M. Williams(4) showed that dimethyl fumarate was a by-product in the bromination catalyzed by hydrogen bromide of dimethyl maleate in carbon tetrachloride in the dark. It is, however, not clear whether dimethyl fumarate was produced by the sole action of hydrogen bromide or oxygen had any influence on it. In the present investigation it has been established that dimethyl maleate is isomerized to the fumarate by the catalytic action of hydrogen bromide and of hydrogen chloride and the presence of oxygen is indifferent to this catalyzed transformation under the present experimental conditions. The effect of reduced nickel, which is much weaker than that of oxygen in the case of isostilbene, has not been examined.

Materials. *Dimethyl Maleate.* 90 Grammes of maleic acid was dissolved in 1200 c.c. of methanol containing 75 g. of concentrated sulphuric acid and the solution was boiled on a water bath for ten hours. Then 450 c.c. of methanol was distilled off, the cooled reaction mixture poured into ice water and extracted repeatedly with carbon tetrachloride. The carbon tetrachloride layer was shaken with aqueous sodium carbonate solution, washed with water, and then dried with anhydrous sodium sulphate. After carbon tetrachloride was distilled off under the ordinary pressure the remaining oil was fractionated through a Widmer column and the middle fraction boiling at 88–88.5° under 6 mm. was collected (n_D^{20} 1.4429).

Hydrogen Bromide. Hydrogen bromide was generated by dropping bromine on hot tetralin, passed through a wash bottle containing tetralin and then through U-tubes filled with anhydrous calcium bromide and with anthracene respectively. For further purification, after bubbled through a bubble counter in which a part of the gas was liquefied by cooling with solid carbon dioxide and ether, the hydrogen bromide was collected in a receiver surrounded by liquid air. Then traces of incondensable gases were eliminated by repeated melting and solidification of the hydrogen bromide and evacuation of the vessel. Finally the gas was fractionated, a middle portion being collected in a gas burette. In some experiments hydrogen bromide was purified by passing through cold tetralin and over moist red phosphorus, anhydrous calcium bromide, and phosphorus pentoxide. It made no difference in the experimental results which of the methods was used in preparing hydrogen bromide.

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(3) Skraup, *Monatsh.*, **12** (1891), 118.

(4) *J. Chem. Soc.*, **1930**, 1059.

Hydrogen Chloride. Hydrogen chloride was prepared from concentrated hydrochloric and sulphuric acids, dried by passing through concentrated sulphuric acid, condensed in a receiver cooled with liquid air, and then fractionated as in the case of hydrogen bromide.

Carbon Tetrachloride. A purest commercial product was boiled with alkaline potassium permanganate solution for six hours, washed with water, dried with calcium chloride, and then distilled over phosphorus pentoxide.

Experimental Procedures and Results. All the experiments were conducted in the dark at room temperature and the extent of reaction was examined under a photographic lamp.

(1) *Isomerization by Hydrogen Bromide.* In a glass tube with a capacity of 7–8 c.c. 0.2 c.c. of dimethyl maleate was taken, the air in the tube was evacuated, hydrogen introduced and again thoroughly evacuated; after the admission of 5 c.c. of hydrogen bromide (the volume of gas refers to the ordinary pressure) the tube was sealed off. In the course of one minute or two dimethyl maleate changed with an evolution of heat into a solid crystalline mass, which was then taken out of the tube by breaking it and crystallized from methanol, melting point 102–103°. In admixture with an authentic specimen of dimethyl fumarate the melting point showed no depression. In some experiments dimethyl maleate contained in a side tube attached to the reaction tube was vacuum-distilled into the latter under the complete exclusion of air, and the side tube having been severed by sealing off, the above-mentioned procedure was pursued; the results were the same. Catechol (5 mg.) added beforehand to dimethyl maleate had no influence on the isomerization by hydrogen bromide, whereas it is quite active in preventing that of isostilbene to stilbene caused by the joint action of hydrogen bromide and oxygen.

(2) *Isomerization by Hydrogen Bromide in Carbon Tetrachloride.* One c.c. of dimethyl maleate and 10 c.c. of carbon tetrachloride (with or without addition of catechol) were pipetted into a glass tube of 65 c.c. capacity, which was evacuated with simultaneous cooling with solid carbon dioxide and ether; the solidified mixture was then melted under evacuation and about 10 per cent of carbon tetrachloride was distilled off, thus traces of air being eliminated from the solution. Then 5–10 c.c. of hydrogen bromide was introduced, the tube sealed off and left to stand in the dark for a certain period. By a capillary seal attached to it the tube was connected to the vacuum line with a piece of rubber tubing, inside which the seal was broken by crushing from without. Introduction of hydrogen and subsequent evacuation enabled the complete removal of hydrogen bromide avoiding the complicating access of air. The carbon tetrachloride solution was washed with aqueous sodium carbonate solution and then with water, and dried over anhydrous sodium sulphate. On distilling off carbon tetrachloride and cooling the remaining mixture, of which Beilstein's test indicated the presence of bromine, dimethyl fumarate crystallized out. Though the experiments were of the qualitative nature the extent of isomerization was approximately estimated by noting the temperature at which the last crystals disappeared when the sample was heated very gradually in a water bath, and determining the composi-

tion from the composition-fusing point curve drawn by R. Schmidt.(5) Some of the results are tabulated in Table 1.

Table 1.

Exp. No.	Hydrogen bromide admitted (c.c.)	Catechol added (mg.)	Reaction time (hours)	Fumarate produced (per cent)
27	10	0	20.5	18
28	10	20	20.5	20
29	5	0	2.5	11
30	5	40	2.5	14

Table 2.

Exp. No.	Hydrogen bromide admitted (c.c.)	Oxygen added (c.c.)	Reaction time (hours)	Fumarate produced (per cent)
47	5	0	5	15
48	5	5	5	13
49	5	0	24.5	20
50	5	5	24.5	19

As the reaction in carbon tetrachloride was much slower than in absence of solvents the effect of oxygen on the reaction could be conveniently examined. In the experiments with added oxygen the reaction mixture, after removal of hydrogen bromide, was immediately evaporated and the composition estimated (Table 2). The increase of the amount of oxygen added up to 50 c.c. had no perceptible influence on the results. In every pair of conjugate runs a difference of one or two per cent in the amount of fumarate produced was observed; in all likelihood this might not be a real difference in view of the experimental accuracy and the conclusion is that oxygen and catechol have no influence on the isomerization caused by hydrogen bromide of dimethyl maleate to the fumarate.

(3) *Isomerization by Hydrogen Chloride.* The experimental details were quite the same as described in (1). It was about one hour before the precipitation of dimethyl fumarate set in and the reaction was slowly brought to completion in the course of more than ten hours. The addition of catechol caused no alteration of the progress of the reaction. In presence of a larger amount of hydrogen chloride the isomerization was of course rapid: in a vessel with a capacity of 65 c.c. 0.2 c.c. of dimethyl maleate and 50 c.c. of hydrogen chloride were sealed; the isomeric ester began to deposit in five minutes, and the conversion was nearly completed in 40–45 minutes.

(4) *Isomerization by Hydrogen Chloride in Carbon Tetrachloride.* The procedure described in (2) was closely followed substituting hydrogen chloride for the bromide. The results are summarized in Table 3.

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(5) *Z. physik. Chem.*, B, **1** (1928), 209.

Table 3.

Exp. No.	Hydrogen chloride admitted (c.c.)	Oxygen added (c.c.)	Reaction time (hours)	Fumarate produced (per cent)
7	5	0	21	4
8	25	0	42	18
9	25	20	42	17

Discussion. Numerous investigations on the isomerization of the maleinoid to the fumaroid compounds are available and the action of halogens which are effective in the light in causing the transformation is attributed to halogen atoms formed by the absorption of light quantum. The inversion is supposed to occur in a molecule formed by the addition of the halogen atom thus produced to the ethenoid linkage, the subsequent elimination of the halogen atom regenerating the isomeric ethenoid form.

M. S. Kharasch, J. V. Mansfield, and F. R. Mayo(6) have observed, that isostilbene is isomerized to stilbene by hydrogen bromide either in the light or in the presence of a peroxidic substance and not by hydrogen bromide alone, that the catalyzed transformation is prevented by anti-oxidants (e.g. hydroquinone, catechol), and that hydrogen chloride is ineffective in causing the isomerization under any of the conditions. Thus they have been led to the belief, that in this reaction the active catalysts are bromine atoms which are produced by the action of a peroxide or light on hydrogen bromide. Further, Y. Urushibara and O. Simamura(1)(2) have reported that oxygen, too, is effective in activating hydrogen bromide to isomerize isostilbene to stilbene.

As detailed in the experimental part of the present communication dimethyl maleate is converted into the fumarate by hydrogen bromide and by hydrogen chloride and the influence of oxygen is not perceptible. However, the possibility of the influence of oxygen cannot totally be excluded. The effect of oxygen, if any, must be negligibly small compared with that of hydrogen bromide alone; but the possibility of the effectiveness of oxygen in the case of hydrogen chloride can readily be ruled out on the basis of the stability of the latter toward oxygen and by the experimental fact that hydrogen chloride and oxygen do not cause the isomerisation of isostilbene. Thus the conversion of dimethyl maleate into the fumarate by hydrogen halides belongs to another type of catalyzed cis-trans isomerization apparently distinct from that of isostilbene by hydrogen bromide and oxygen.

Concerning the mechanism of the conversion of maleic into fumaric acid caused by aqueous hydrogen halides several speculations are available. From a kinetic study of the reaction E. M. Terry and L. Eichelberger(7) have proposed a hypothesis, that the catalyst goes into interaction with carboxyl groups and "saturates" them, and that this removes the stabilizing influence of the carboxyl group upon the double bond, facilitating the

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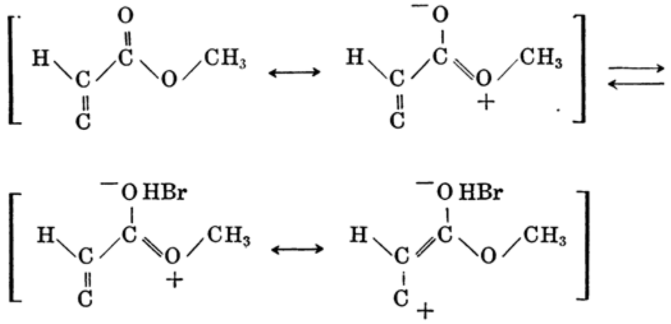
(6) *J. Am. Chem. Soc.*, **59** (1937), 1155.
(7) *J. Am. Chem. Soc.*, **47** (1925), 1402.

activation of the latter to the isomeric change. This idea of the interaction of the group adjacent to double bond with the catalyst may be applicable to account for the mechanism of the isomerization of dimethyl maleate under consideration, because hydrogen halides do not isomerize isostilbene but dimethyl maleate, and it seems highly probable that the carbomethoxyl group plays an important role. Moreover, as the experiments have been made either without solvents or in non-hydroxylic one, the hypothesis can be stated in a more concrete form: the association of the ester group with hydrogen halides by means of, for example, hydrogen bond formation deforms more or less the electronic configuration of the molecule, and thus destroys the rigidity of the double bond. In support of the idea that the addition of the acids to ester group takes place, a work of O. Maass and D. McIntosh⁽⁸⁾ may be cited, who confirmed the existence of an addition compound $CH_3CO_2C_2H_5{\cdot}HBr$, and further W. Gordy and P. C. Martin⁽⁹⁾ concluded the formation of hydrogen bond between hydrogen chloride and ethyl acetate from a study of the infrared absorption spectra.

It seems to be hardly possible, that the addition should take place at the oxidic oxygen as W. A. Waters⁽¹⁰⁾ seems to believe, because then this oxygen atom would have to gain in positive charge against the opposing influence of the carbonyl group. On the other hand, if in the carboxylic ester molecule the resonance effect is considerable as contended by S. Mizushima and M. Kubo,⁽¹¹⁾ more negative charge will concentrate on the carbonyl oxygen atom than otherwise; thus the association with hydrogen halides may take place through the carbonyl oxygen, and the subsequent activation of the double bond as formulated below:



The formation of co-ordination link through hydrogen atom and carbonyl group prior to the isomerization has already been postulated by G. R. Clemo and S. B. Graham⁽¹²⁾ who have noticed the catalytic action of primary and secondary amines, especially of piperidine, on the isomerization of dimethyl maleate. Their assumption seems to be appropriate in view of the analogy between the catalytic actions of piperidine

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(8) *J. Am. Chem. Soc.*, **34** (1912), 1272.

(9) *Phys. Rev.*, **52** (1937), 1075.

(10) W. A. Waters, "Physical Aspects of Organic Chemistry," 2nd Ed., 266, London (1937).

(11) This Bulletin, **13** (1938), 174.

(12) *J. Chem. Soc.*, **1930**, 213.

and hydrogen halides, the former, too, being ineffective in causing the transformation of isostilbene to stilbene as confirmed by the present author.

Summary.

(1) No isomerization of isostilbene to stilbene occurs with hydrogen chloride in the presence of either reduced nickel or oxygen.

(2) Hydrogen bromide and hydrogen chloride cause the isomerization of dimethyl maleate to the fumarate either in absence of solvents or in carbon tetrachloride solution.

(3) Oxygen has no effect on the isomerization of dimethyl maleate by hydrogen halides.

(4) The isomerization of dimethyl maleate by hydrogen halides belongs to another type of catalyzed cis-trans isomerization apparently distinct from that of isostilbene by hydrogen bromide and oxygen.

(5) A hypothesis has been proposed concerning the mechanism of the isomerization of dimethyl maleate caused by hydrogen halides.

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