

XXIV.—*On the action of Hydrobromic Acid and of Hydriodic Acid upon Polyatomic Acids, and on the behaviour of the Iodo-substitution compounds towards Hydriodic Acid.*

By AUG. KEKULÉ.

FORMERLY in considering organic acids, importance was attached only to their basicity ; but latterly, and I believe I was the first who drew the attention of chemists to this subject, besides their basicity, their atomicity has also been taken into consideration. Three kinds of hydrogen are therefore distinguished in organic acids, according to the part it plays : 1st. Hydrogen which belongs to the radicle, according to the expression of the theory of types.

2nd. Typical Hydrogen. The latter is either easily substituted by metals (hydrogen of acids), or it does not possess this property (hydrogen of alcohols). Those polyatomic acids, whose basicity is less than their atomicity, stand, as regards the nature of the typical atoms of hydrogen, between the alcohols and those organic acids whose basicity is equal to their atomicity.

The cause of the difference between the typical hydrogen-atoms must be sought in the nature of those atoms which surround the respective hydrogen-atoms. It is, in fact, very apparent that the chemical nature of the place which these hydrogen-atoms occupy, must be the resultant of all the forces of attraction which the various atoms surrounding this place exercise.

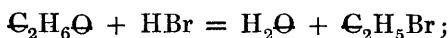
According to the theoretical views which I formerly published, that hydrogen which, according to the theory of types, belongs to the radicle, stands in direct relation to the carbon-atom ; the typical hydrogen is, on the contrary, in combination with the carbon-group, only through the mediation of oxygen. This typical hydrogen is easily substituted by metals, if there happens to be in its neighbourhood an atom of oxygen which is completely combined with carbon ; if this is not the case, it has the behaviour of the typical hydrogen of the alcohols.

It will, therefore, be easily understood why, in glycollic and other polyatomic acids, whose basicity is less than their atomicity, the typical atoms of hydrogen are not absolutely of the same value. Such substances behave as though one side of the molecule were composed of an alcohol, and the other of an acid.

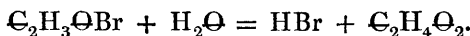
I have elsewhere explicitly shown that all known facts relating to

this class of acids admit of, a simple explanation by this theory, and several chemists have since brought forward numerous observations, which, however, tend further to support it. But as the typical, but not acid, hydrogen-atoms of these acids are thus confounded by some chemists with the typical hydrogen-atoms of the alcohols, it appears to me to be appropriate to support my views by other facts.

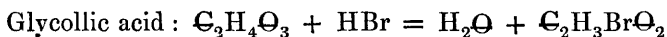
It is now well-known that one of the most characteristic differences between alcohols and acids, is the facts that alcohols produce bromides or chlorides when acted upon by hydrochloric or hydrobromic acid,



whereas with acids the same reaction takes place in precisely an inverted sense, so that the chloride or bromide undergoes decomposition by water; for example:



If now in glycollic acid and lactic acid, one side of the molecule behaves like an alcohol, these acids ought to exhibit the same behaviour as the alcohols with hydrobromic acid; they ought therefore to form the corresponding bromide by losing water. These bromides are well known to be identical with the products of substitution by bromine in acetic acid and propionic acid. The same bodies which, until now, have been obtained as products of substitution from acetic acid or propionic acid, ought therefore to be producible as ethers from glycollic and lactic acids.

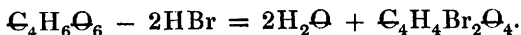


In the same manner the formation of monobromosuccinic acid was to be expected from the dibasic and triatomic malic acid:



Bromosuccinic acid.

In a similar manner, dibromosuccinic acid might have been formed from the dibasic and tetratomic tartaric acid containing two alcoholic hydrogen-atoms:

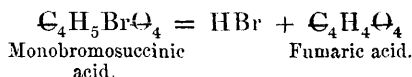
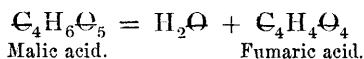


The experiments which I have made up to the present time have confirmed this opinion for all those acids which contain only one atom of alcoholic hydrogen.

*Glycollic Acid.*—When glycollic acid (formed by oxidation of alcohol) is heated to  $100^{\circ}$  with a cold concentrated aqueous solution of chemically pure hydrobromic acid, monobromacetic acid is produced. The monobromacetic acid thus obtained, boils at  $205^{\circ}$  to  $208^{\circ}$ , and congeals in the condensing tube to a crystalline mass. By treating it with sodium-amalgam, it could be transformed into acetic acid; by boiling with lime and water, it regenerated glycollic acid; by acting upon it with an alcoholic solution of ammonia, glycecoll was easily produced.

*Lactic Acid.*—Under the same conditions, lactic acid forms bromopropionic acid. This acid boils at  $202^{\circ}$  (corrected  $205^{\circ}5$ ), and congeals in a freezing mixture ( $17^{\circ}$ ) to a laminar crystalline mass. It forms propionic acid when treated with sodium-amalgam; when boiled with oxide of zinc, it yields lactate of zinc containing the same amount of water as the zinc-salt of ordinary lactic acid; when it is heated with an alcoholic solution of ammonia, alanine is readily formed.

*Malic Acid.*—This acid exhibits the same behaviour. On heating it to  $100^{\circ}$  with fuming hydrobromic acid for some hours, a considerable quantity of monobromosuccinic acid is formed. The acid thus produced appears to me to be identical with the monobromosuccinic acid which I formerly produced by acting upon succinic acid with bromine; I cannot, however, decide this question with absolute certainty. It forms small crystals, easily soluble in water, alcohol, and ether (1 part in 5.2 parts of water of  $15^{\circ}5$ ). It melts at  $159^{\circ}$ — $160^{\circ}$ , and is slowly decomposed even at this temperature, more quickly when heated more strongly, forming fumaric and hydrobromic acids. Bromosuccinic acid is therefore decomposed in a manner exactly similar to malic acid, of which it may be regarded as a hydrobromic ether:



Monobromosuccinic acid when acted upon by sodium-amalgam

easily yields succinic acid, which appears to be perfectly identical with ordinary succinic acid. It is decomposed with extraordinary facility by oxide of silver. The malic acid thus obtained is optically inactive, and appears to be identical with the inactive malic acid obtained from inactive aspartic acid. When monobromosuccinic acid is heated with an aqueous or alcoholic solution of ammonia, various amides are formed, one of which appears to be aspartic acid. From the facts here enumerated, we may conclude, with tolerable probability, that other polyatomic acids, containing only *one* atom of alcoholic hydrogen, will show the same behaviour.

For those polyatomic acids which contain *two* atoms of alcoholic hydrogen, the behaviour appears to be different. I have at least not been able to produce dibromosuccinic acid from tartaric acid; I obtained rather a comparatively small quantity of monobromosuccinic acid. Racemic acid exhibits precisely the same deportment. I shall, upon some future occasion, again refer to this formation of monobromosuccinic acid, and will here only mention that it is perfectly analogous to the formation of monoiodopropionic acid from glyceric acid.

I have hitherto studied the above-mentioned reaction, chiefly with hydrobromic acid, but I have proved qualitatively that hydrochloric acid shows a perfectly analogous behaviour. It might, therefore, be concluded that hydriodic acid would produce the same reaction; and if no substitution-products of acids containing less oxygen, are formed thereby, the cause of this negative result must be sought in a peculiar behaviour of iodo-substitution-compounds, of which I am now going to treat.

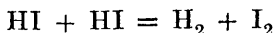
*On the Action of Hydriodic Acid upon Iodo-Substitution-Compounds.*

Iodine, though generally speaking very similar in its behaviour to chlorine and bromine, shows, nevertheless, some differences worthy of remark. In general it acts much less energetically, and it never produces substitution-compounds, when acting, for example, upon organic substances. Many compounds of iodine have, on the contrary, the property of being easily decomposed, with liberation of iodine.

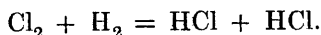
This difference between iodine on the one hand, and chlorine and bromine on the other, shows itself even in the simplest compounds, in its combination with hydrogen, for example.

Chlorine combines easily with hydrogen, and forms hydrochloric acid; hydriodic acid is, on the contrary, easily decomposed into iodine and hydrogen. Both reactions may be expressed by the same equation, but the decomposition takes place with chlorine in one sense, with iodine in the other.

For iodine we have :



for chlorine :



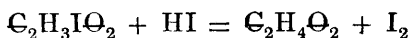
From a theoretical point of view, it appeared probable that this peculiarity of iodine might be found in all its compounds, and that, in many cases, in which chlorine produces a definite reaction, a precisely contrary reaction would be produced by iodine.

I presumed, amongst other things, that iodo-substitution-compounds would be decomposed by the action of hydriodic acid, so as to form the normal substances, with liberation of iodine, by an inverse substitution process.

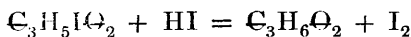
The experiments hitherto made, have confirmed my expectation. I shall for the present confine myself to mentioning the results which I have obtained with iodo-substitution-compounds corresponding to organic acids.

When iodoacetic acid (prepared according to the method of Perkin and Duppa) is brought into contact with a concentrated aqueous solution of hydriodic acid, reaction takes place, even in the cold, iodine being liberated and acetic acid formed.

The iodo-propionic acid, prepared according to Beilstein's method, by the action of iodide of phosphorus ( $P_2I_4$ ), on glyceric acid, is likewise acted upon by hydriodic acid, but the action does not take place till about  $180^\circ$ , at which temperature propionic acid is formed. Both decompositions may be explained by the following equations :



Iodoacetic  
acid.



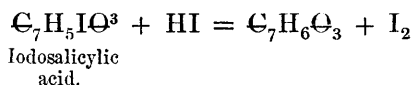
Iodopropionic  
acid.

If this action of hydriodic acid on the iodo-substitution-compounds of organic acids proves to be of a general character, as from theoretical reasons I believe it to be, it becomes evident

that iodo-substitution-compounds can never be formed by the direct action of iodine upon organic acids.

Now since, according to experiments made by Kolbe and Lautemann, and afterwards followed up by Lautemann alone, iodosalicylic acid is directly obtained by heating salicylic acid with iodine, it appeared to me to be of special interest to expose the iodosalicylic acid thus obtained to the action of hydriodic acid.

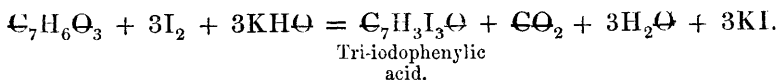
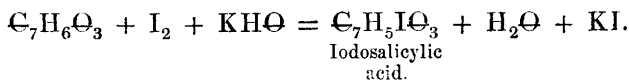
I have found that the mono-iodosalicylic acid produced by Lautemann's method, is easily attacked by hydriodic acid. The action takes place even below 100°, iodine being liberated, and salicylic acid formed, according to the equation :



It is, therefore, evident that iodosalicylic acid cannot possibly be formed by the direct action of iodine upon salicylic acid, as Kolbe and Lautemann assert. Indeed, it is easy to see that the iodosalicylic and iodophenylic acids are produced by other reactions, and that nearly all that Kolbe and Lautemann state upon the formation of these acids, is based upon erroneous observations.

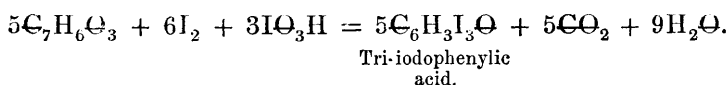
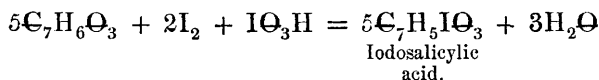
It would lead me too far to describe here all the experiments that I have made in order to throw some light upon the formation of the iodated acids described by Lautemann. I, therefore, confine myself to the following observations :—When salicylic acid is melted with iodine, or boiled with iodine and alcohol, no reaction takes place ; and this explains why Lautemann could nowhere find the hydrogen which the salicylic acid must have necessarily eliminated. The iodosalicylic and the iodophenylic acids are formed by the process which Lautemann employed to separate the bodies which he fancied were already formed. In this process, two reactions must be distinguished, both of which lead to the formation of products containing iodine, of which fact I have convinced myself by special experiments.

When iodine acts upon an alkaline solution of a salicylate, iodosalicylic acids are principally formed, as also the red body described by Lautemann ; at the same time, small quantities of iodophenylic acids are obtained. The formation of these products may be illustrated by the following formulæ :



The second reaction by which products containing iodine may be produced from salicylic acid, is as follows:—When iodine acts upon salicylic acid in presence of iodic acid, salicylic acids containing iodine, and more especially iodo-substitution-compounds of phenylic acid, are formed.

We have for example :



That iodophenylic acids are the chief products of this reaction, is explained by the behaviour of salicylic acid and iodosalicylic acid to iodic acid. When salicylic acid is heated with water and iodic acid, decomposition takes place even below  $100^\circ$ , phenylic and carbonic acids being produced. It will be easily understood that, in both reactions, products containing iodine may be formed. The hydrogen of salicylic acid is not taken away by iodine, to form hydriodic acid, but is expelled in each reaction in the form of water. The conditions which prevent the formation of iodo-substitution-compounds by the direct action of iodine are consequently evaded.

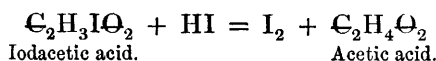
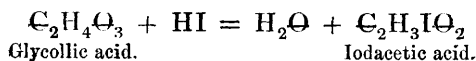
#### *On the action of Hydriodic Acid upon Polyatomic Acids.*

The observations above enumerated lead to a simple theory of the beautiful reaction first brought into use by Lautemann, which has since rendered possible the reduction of many organic acids. The reduction caused by hydriodic acid is explained in the following manner: The reaction takes place by two stages; in the first stage, hydriodic acid produces a hydriodic ether, with elimina-

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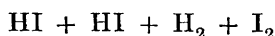
tion of water, that is to say, an iodo-substitution-compound of the same series of oxidation, containing less oxygen. In the second stage, this product of substitution by iodine is carried over into the normal substance by hydriodic acid acting by inverse substitution.

We have for example :



If we take into consideration that iodacetic acid is attacked even by dilute hydriodic acid at a low temperature, whereas the action of hydriodic acid on glycollic acid evidently does not take place, except under the same conditions as with hydrobromic acid (that is to say, by using a concentrated solution, and by heating), it is easy to perceive that the iodacetic acid which is formed as intermediate product, cannot be detected. It is evident that in all such reactions, no matter in what proportions the substances in question may be employed, the intermediate products can be detected only when they are less easily attacked by the reagent employed than the original substance. It will be further more comprehensible why only polyatomic acids whose basicity is less than their atomicity, are reduced by hydriodic acid. The reduction necessitates the formation of a hydriodic ether (an iodo-substitution-compound), and can, therefore, take place only with substances which contain alcoholic hydrogen.

I will finally observe that the typical reaction above mentioned,

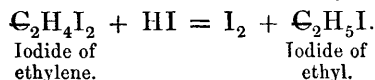
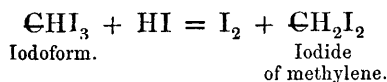


which can be more generally expressed in the following form :



appears to me to be susceptible of a further extension in various directions. I may perhaps be permitted to mention here some of the experiments on which I am at present engaged. Hydriodic acid may be allowed to act upon bodies which do not contain oxygen; retrograde substitutions would then be produced as follows :





Organic iodides may be employed instead of hydriodic acid, and thus syntheses similar to the following may probably be realised :

