gases, is destroyed by agitation with a large quantity of water; it is also, contrary to the common statements, destroyed by being agitated with lime-water and baryta-water, provided a sufficient quantity of those solutions be used; it has always the same peculiar odour; it bleaches without producing previously an acid reaction; it oxidizes in all cases the same bodies, &c.

From the whole investigation the author draws the conclusion, "that ozone, from whatever source derived, is one and the same substance, and is not a compound body, but oxygen in an altered or allotropic condition."

XIII. "On Rubian and its Products of Decomposition."—Part III. By Edward Schunck, F.R.S. Received June 13, 1855.

Combined Action of Alkalies and Oxygen on Rubian.

In the preceding part of this paper the author has shown that the action of alkalies is essentially the same as that of acids on rubian, the only difference being that the rubianine produced by acids is replaced by rubiadine when alkalies are employed. Now though this is in all cases the final result of the action of alkalies, there still remained a possibility of the existence of bodies intermediate between rubian and the final products of decomposition. Such bodies do in reality exist, but their formation is dependent, in part at least, on the simultaneous action of oxygen.

When alkalies or alkaline earths, as potash, soda, ammonia, baryta or lime, or the bicarbonates of baryta or lime are added to a watery solution of rubian, and the solution is exposed to the air, oxygen is absorbed, and three distinct bodies are formed, to which the author has given the names of *Rubianic Acid*, *Rubidehydran* and *Rubihydran*. The method of separating these bodies and obtaining them in a state of purity is fully detailed. Even oxide of lead is a sufficiently strong base to cause rubian to undergo this process of decomposition in the presence of oxygen. From this cause the lead compound of rubian, after being exposed for some time to the atmosphere, no longer contains unchanged rubian, but products of its decomposition; and hence also it follows that in the processes pro-

posed by Kuhlmann, Berzelius and others for the preparation of the so-called xanthine, and in that of Rochleder for the preparation of his ruberythric acid, all of which depend on the use of alkaline earths or basic acetate of lead, products of decomposition of rubian must in every case be formed. Besides the substances just mentioned, a little acetic acid, and sometimes also rubiadine, and sugar in small quantities are formed. Whether the first is an essential product of decomposition or not, the author leaves undecided; but the other two he considers as decidedly secondary products, resulting from the decomposition of rubidehydran or rubihydran.

Rubianic acid is soluble in water and alcohol, but not in ether. It crystallises in lemon-yellow silky needles. Its watery solution has a distinctly but not strongly bitter taste. When heated it yields a sublimate of alizarine. By the action of strong acids, as well as of caustic alkalies and of erythrozym, it is decomposed into alizarine and sugar. Its compounds with potash and ammonia crystallize in small puce-coloured needles. The soda salt is deposited from the watery solution as a mass of small red spherical grains, which are very sparingly soluble in water. These compounds possess very little stability. The baryta and lime salts are obtained by double decomposition as red precipitates. The acid is completely precipitated from its watery solution by basic acetate of lead, the precipitate being red, and resembling that produced by the same salt in a solution of rubian.

The composition of rubianic acid is expressed by the formula

$$C_{52}H_{29}O_{27},$$

that of the potash salt by

$$C_{52}H_{28}O_{26}+KO,$$

that of the neutral baryta salt by

$$C_{52}H_{28}O_{26}+BaO+HO.$$

The conversion of the acid into alizarine and sugar is symbolized by the following equation:—

$$C_{52}H_{29}O_{27}+5HO=2C_{14}H_5O_4+2C_{12}H_{12}O_{12}.$$

In order to leave no doubt regarding the correctness of the formula, the author determined the quantity of alizarine formed by the decomposition of the acid. According to calculation, 100 parts of acid should yield 43·44 parts of dry alizarine. In two experiments the author obtained 42·47 and 45·17 per cent. of alizarine.

The presence of oxygen is necessary for the formation of this acid. If a watery solution of rubian made alkaline with soda or baryta be kept out of contact with the air, no rubianic acid is produced, whereas an abundance of the latter is obtained from the same solution on exposure to the atmosphere. The manner in which it is formed from rubian may be represented by the following equation :—

$$C_{56}H_{34}O_{30}+10O=C_{52}H_{29}O_{27}+4CO_2+5HO.$$

The author considers this as the first known instance of a body, belonging to the class of glucosides, or conjugate compounds containing sugar, having been observed to form by a process of oxidation.

The author thinks it probable that this acid and the ruberythric of Rochleder are identical, but the description given of the latter by the discoverer is not sufficiently minute to enable him to come to a decision on this point. Rochleder has moreover given a very different composition for his acid. Until the properties and composition of the latter have been more accurately investigated, the author prefers considering the two acids as distinct. If they are identical, then Rochleder has merely committed the common error of mistaking a product for an educt.

Rubidehydran and rubihydran have both properties very nearly resembling those of rubian, from which they can only with difficulty be distinguished. Neither of them however is capable of yielding rubianic acid when treated in the same way as rubian. The composition of rubidehydran is expressed by the formula

$$C_{56}H_{32}O_{28},$$

that of rubihydran by

$$C_{56}H_{39}O_{35}.$$

The former contains therefore the elements of 2 equivs. of water less the latter, the elements of 5 equivs. of water more than rubian. Both substances give, when decomposed by strong acids, the same products, viz. alizarine, rubiretine, verantine, rubiadine and sugar. The products formed by acids are therefore the same as those produced from rubian by alkalies, which renders it probable that the latter, when acted on by alkalies, is first converted into rubidehydran or rubihydran, or both.

Rubiadine may be obtained from rubihydran in large quantities

and in a state of great purity, and the author had thus an opportunity of examining the properties and composition of this substance more accurately than heretofore. From the new analyses which he made he infers that its formula is

$$C_{32}H_{13}O_9,$$

which differs from

$$C_{32}H_{12}O_8,$$

the one formerly given, by 1 equiv. of water.

Action of Chlorine on Rubian.

When chlorine gas is passed through a watery solution of rubian, the solution deposits lemon-yellow or orange-colour flocks and becomes colourless. The flocks consist of a peculiar substance, which the author calls *Chlororubian*. The liquid contains sugar. Chlororubian crystallizes from its solution in alcohol in small orange-coloured needles. It is soluble in boiling water, but not as easily as in alcohol. On being heated, however carefully, it is decomposed. It is dissolved by caustic and carbonated alkalies, forming blood-red solutions. The baryta and lime compounds are red and insoluble. The watery solution produces with basic acetate of lead a light red precipitate. The author gives for the chlororubian the formula

$$C_{44}H_{27}ClO_{24}.$$

Its formation from rubian is represented by the following equation :—

$$C_{56}H_{34}O_{30}+6HO+2Cl=C_{44}H_{27}ClO_{24}+C_{12}H_{12}O_{12}+2ClH.$$

Chlororubian is decomposed by strong acids and splits up into sugar and another body, which has the formula

$$C_{32}H_{12}ClO_9,$$

and which, in consequence of the relation in which it stands to rubiadine, the author calls *Chlororubiadine*. The manner in which this process of decomposition takes place will be seen from the following equation :—

$$C_{44}H_{27}ClO_{24}=C_{32}H_{12}ClO_9+C_{12}H_{12}O_{12}+3HO.$$

Chlororubiadine is soluble in alcohol. The boiling solution deposits it on cooling in yellow shining needles. It is insoluble in boiling water. It is not decomposed by dilute nitric acid or on boiling, but nitric acid of sp. gr. 1·52 dissolves, and on boiling

decomposes it, and nitrate of silver now gives a precipitate of chloride of silver. Chlororubiadine dissolves in caustic and carbonated alkalies with a red colour. With baryta it gives a compound, crystallizing in long red needles. The author did not succeed in converting rubiadine into chlororubiadine, nor, on the other hand, was he able to substitute the chlorine of the latter by hydrogen, and thus form rubiadine.

The sugar which is formed from chlororubian, together with chlororubiadine, may be obtained in a crystallized state, when it has the properties and composition of crystallised grape-sugar.

When chlororubian is treated with caustic soda, the chlorine is entirely separated, forming chloride of sodium. The other products of decomposition are verantine, rubiretine, a body resembling rubiadine, sugar, and a yellowish-brown substance insoluble in water, in alcohol, and even in alkalies, the probable formula of which is

$$C_{44}H_{14}O_{12},$$

and for which the author proposes the name of *Oxyrubian*, since it owes its formation to the chlorine of chlororubian being replaced by oxygen.

By the continued action of chlorine chlororubian is converted into a white body, which the author calls *Perchlororubian*. This body is insoluble in water and caustic alkalies, but soluble in alcohol and ether. It crystallizes from the alcoholic solution in colourless, transparent, four-sided tables, exhibiting a beautiful iridescence. When carefully heated it may be entirely volatilized. It is not decomposed by nitric acid of sp. gr. 1·52, even on boiling, but is merely dissolved. Its composition is expressed by the formula

$$C_{44}H_{9}Cl_{9}O_{15}.$$

From these experiments it follows that chlororubian is a conjugate body containing sugar. In this respect it resembles Piria's chlorosalicine.

In all processes of decomposition previously described rubian yields three series of compounds, just as if it consisted of three bodies. When acted on by chlorine, however, it yields only one series of products, which corresponds exactly with one of the three series of the other processes, the bodies belonging to the two other series not making their appearance, even in the form of products of substitution.