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I. *On the Iodide of a new Carbo-hydrogen.* By JAMES  
F. W. JOHNSTON, F.R.S.\*

IF coal gas be made to pass slowly and for a length of time over pure iodine, the latter substance moistens, and is partly changed into a dark-brown liquid, which effervesces with alkaline carbonates, showing the presence of hydriodic acid. After some hours, colourless prismatic crystals shoot out from the iodine, and clothe the interior of the vessel, and ultimately the whole is changed into a mixture of different compounds forming an olive-coloured substance, partly coating thickly the sides of the vessel, and partly constituting an unctuous mass, with the dark fluid at the bottom.

The liquid contains free iodine and hydriodic acid. When washed out from the solid portion by alcohol and neutralized by caustic potash, the solution gives a yellow precipitate, consisting of a mixture of Faraday's iodide of carbo-hydrogen ( $H_2 C_2 I$ )† and of iodide of formyle (iodoform  $H C_2 I_3$ ).

The solid product being exposed to the air loses its unctuousity. If broken up and examined by the microscope it is seen to consist of a congeries of colourless prisms ( $H_2 C_2 I$ ) mixed with another substance, which is amorphous, and of a dark green almost black colour. Alcohol separates the former, or if the mixture be exposed to the air they volatilize, leaving the dark green substance nearly pure.

The production of the hydriodic acid and of the iodides of formyle and of carbo-hydrogen is easily understood. Coal gas contains probably more than two equiatomic compounds of carbon and hydrogen; at least two,  $C H_2$  and  $C_2 H_2$ , the

\* Communicated by the Author.

[† Mr. Faraday's account of this substance will be found in *Phil. Mag.* First Series, vol. lix. p. 352. EDIT.]

light carburetted and olefiant gases, are present. The latter would furnish the three compounds obtained in this experiment, as shown by the following formula :



that is to say, one atom of olefiant gas decomposes to form hydriodic acid and formyle, while another unites with iodine\* directly. Still this does not represent the action *quantitatively*, since the proportion of the  $C_2 H_2 I$  is much greater in actual experiment, and appears also to be variable.

Such is the action in close vessels provided only with a small aperture to allow the current of gas to pass out very slowly; but since these three compounds are all volatile, it is easy to understand how only the solid dark green fixed substance should be obtained when the iodine is placed in an open vessel and a current of coal gas is made to stream upon it. In this way it was first obtained by Mr. Kemp of Edinburgh, to whom the discovery of this substance is due, and who several years ago presented me with a specimen prepared by exposing iodine for several days to the action of an open jet of coal gas. I am not aware how far Mr. Kemp has since studied the action in close vessels.

I. This substance is of a dark olive green colour, is without taste, emits a slight odour of naphtha, is brittle, and has a density of about 0.95. It is insoluble in water, and in boiling alcohol or æther. Treated with hot nitric acid it becomes yellow and dissolves. With muriatic acid either in the form of gas or of liquid acid, it undergoes no change. Sulphuric acid aided by heat decomposes it. It blackens and gives off iodine vapour and sulphurous acid, leaving undissolved a very bulky charcoal. Dry chlorine slowly changes its colour to a dark brown. If previously moistened with alcohol it becomes

\* During the combination of chlorine with olefiant gas a portion of muriatic acid is formed, a fact inconsistent with the idea of a *direct* union of the two substances to form  $H_2 C_2 Cl$ : may not an equivalent proportion of the volatile chloroform be produced, as in the above formula, substituting Cl for I? Felix d'Arcet (*Ann. de Chim. et de Phys.*, lxvi. p. 108.) has stated, that during this action of chlorine on olefiant gas, a second oily liquid is formed, represented by  $C_4 H_4 Cl O$ , to which he gives the name of *chloretheral*, but which Berzelius with great probability I think, considers to be a compound of the chloride with the oxide of *clayle* ( $C_2 H_2 Cl + C_2 H_2 O$ ). This explanation of the production of muriatic acid, however, implies that the gases employed are always more or less moist. Regnault accounts for the presence of the acid by representing the oily compound by the rational formula ( $C_2 H_3 Cl + H Cl$ ) part of which is decomposed during the process, and  $H Cl$  evolved. But Löwig and Wiedman have shown that  $C_2 H_3$  (acetylene) does not preexist in the oil, though it may possibly be formed by its decomposition. See Poggendorff's *Annalen*, xlix. p. 133.



yellow by the action of chlorine. In hot solutions of carbonated alkalies it is partly decomposed, iodine being separated, but its colour remains unchanged. Heated to 212° Fahr., it slowly but sensibly loses weight, evolving the odour of naphtha and a little iodine. At a higher temperature it gives off a volatile combustible liquid resembling naphtha, which burns with much smoke, and if the heat be still increased, iodine vapour appears in large quantity colouring the naphtha (?) dark brown, and a bulky shining charcoal remains behind. It is not unlikely that hydriodic acid may also be among the products.

Burned with oxide of copper this substance gave the following results :

1. 8.77 grs. gave  $\ddot{C}$  = 18.56 and  $\dot{H}$  = 4.94 grs.
2. 8.77 grs. gave  $\ddot{C}$  = 18.15 and  $\dot{H}$  = 4.855 grs.
3. 6.137 grs. gave  $\ddot{C}$  = 12.316 and  $\dot{H}$  = 3.505 grs.

These are equivalent, per cent., to

	1.	2.	3.
Carbon.....	= 58.203	57.225	55.490
Hydrogen	= 6.258	6.151	6.346
Iodine.....	= 35.539	36.624	38.164
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100	100	100

It was not till I observed the discrepancy between the first and second analyses that I studied the action of a temperature of 212° Fahr. on this compound, and found that it was slowly decomposed, and iodine expelled from it by this degree of heat. The third analysis therefore was made with more precaution, and care was taken to avoid decomposition by the application of heat while pumping out the moisture from the oxide of copper. In this analysis therefore the chances of error were least, and the result agrees very closely with the formula  $C_{30} H_{20} I_1$  since

	Calculated.	Experiment.
30 carbon... = 2293.110	55.667	55.490
20 hydrogen = 249.592	6.059	6.346
1 iodine.... = 1578.290	38.274	38.164
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	4120.992	100
	100	100

The excess of hydrogen is due to the more imperfect manner in which it was necessary to pump out the water in order to avoid the separation of iodine, as had probably been the

case in the previous analysis\*. The experimental result however may be reconciled to the formula ( $C_{30}H_{20} + HI$ ) which gives 6.340 of hydrogen per cent., a quantity so near to that found as to leave nothing for the ordinary error of analysis. The action of chlorine hereafter described, if the results are to be depended upon, gives a probability to this formula, in addition to that which is derived from the rational formula, adopted by Liebig to represent the constitution of what by other chemists are still regarded as chlorides and iodides of olefiant gas (elayle) and some other carbo-hydrogens.

It has been already stated, that when boiled in carbonated alkalies the colour of this compound remains unchanged, and that it undergoes decomposition. The decomposition however is only partial. 4.51 grs. boiled in a concentrated solution of carbonate of soda, and afterwards washed and dried at a gentle heat, still weighed 3.51 grs. having lost 22.17 per cent. The whole of the iodine therefore is not separated by this process; it may however be completely separated by mixture with pure carbonate of soda, and gradually heating over the lamp to a temperature below redness.

In this way I obtained by means of nitrate of silver an approximation to the quantity of iodine, which however was too rude to be worthy of insertion in the present paper. I was, at the time of making the experiment, unacquainted with the more perfect method of estimating the quantity of iodine since published by Lassaigne.

II. Diffused through water and subjected to the action of chlorine, the green colour of this compound is slowly changed to brown, but the action is much more rapid and complete when the iodide is reduced to fine powder, diffused through alcohol, and submitted to a current of chlorine. Thus treated it speedily acquires a bright yellow colour, combining with chlorine and yielding the iodine to the supernatant liquid, in which it is readily recognised.

I subjected to analysis a portion of the substance thus prepared, after washing with alcohol and drying at  $212^{\circ}$  Fahr. When heated in a close tube it gave off no iodine.

a. 8.45 grs. gave  $\ddot{C} = 18.81$  grs. and  $\dot{H} = 4.545$  grs.

\* 2.795 grs. heated to  $212^{\circ}$  for some time, lost 0.295 gr., and at a subsequent weighing the loss amounted to 0.485 gr. Still it seems possible to preserve it for a long time at ordinary temperatures and in close vessels without sensible decomposition. One of the specimens employed in the above analysis was prepared by Mr. Kemp, and had been in my possession several years.



The water in the chloride of calcium tube reddened litmus, indicating the presence of muriatic acid, by which the weight of water would be in some measure increased.

b. 7.61 grs. heated with dry carbonate of soda, gave 7.033 grs. of chloride of silver or 22.8 per cent. of chlorine.

c. 4.462 grs. heated in like manner, but with more care, gave 4.517 grs. of chloride of silver or 24.12 per cent. of chlorine.

These results give for the composition of the yellow matter

	A	B	
Carbon...	= 61.55		= 30 atoms.
Hydrogen	5.98		17.8 —
Chlorine...	24.12	22.8	2.02 —
Oxygen ...	8.35		3.11 —
	<hr style="width: 50%; margin: 0 auto;"/>		
	100		

This result indicates the irrational formula  $C_{30} H_{17} Cl_2 O_3$ , which gives

30 carbon =	2293.11	=	62.13 per cent.
20 hydrogen	212.15		5.75 —
2 chlorine	885.30		23.99 —
3 oxygen	300.00		8.13 —
	<hr style="width: 50%; margin: 0 auto;"/>		
	3690.56		100.

The elements contained in the above irrational formula are capable of being arranged in several rational positions.

The green iodide being  $C_{30} H_{20} + I$ ,

The yellow substance may be  $(C_{30} \frac{H_{17}}{O_3} + Cl) + Cl$  (1), in which three of hydrogen are replaced by three of oxygen, the atom of iodine by one of chlorine, and the whole combined with another atom of chlorine—the oxygen being derived from the alcohol, which was undergoing a simultaneous decomposition by the action of chlorine.

Or, it may be  $C_{30} \frac{H_{16}}{Cl} O_3 + H Cl \dots$  (2.)

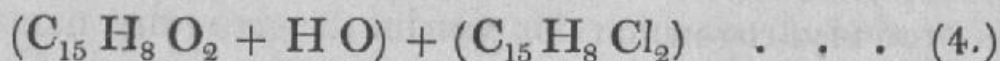
Or —  $C_{30} \left\{ \begin{array}{l} Cl_2 \\ H_{16} + H O \\ O_2 \end{array} \right. \dots$  (3.)

in both of which the principle of substitution is equally evident. Were we to represent the green compound by  $C_{30} H_{20} + H I$ , there would even be a conservation of the original *type* of composition\*. This type may also be supposed to be sufficiently preserved in the radical, and that it is owing

[\* See the memoir of M. Dumas, p. 442 of the last volume.—EDIT.]

to the presence of much muriatic acid in the solution, derived from the action of the chlorine on the alcohol, that this radical  $\frac{30}{20}$  R unites with H Cl ( $2^\circ$ ) instead of simply with Cl, when it might have been represented by a formula \* the exact counterpart of that which indicates the substance from which it is derived.

There is, however, still another mode of representing the rational constitution of this substance, which while it is accordant with the *facts* on which Dumas's views are founded, is inconsistent with the *principle* of the conservation of types. The yellow compound may be



consisting of equal atoms of an analogous oxide and chloride of the radical  $C_{15} H_8$  or  $C_{30} H_{16}$ , with the former of which is combined also an atom of water. This mode of representing it is accordant with the views of Berzelius, and is supported by many interesting and striking analogies.

We ought indeed to distinguish carefully between the *fact* of the mutual substitution of hydrogen and chlorine, and the *theory* of the persistence of types, or the opinion that the element which replaces performs the same function in the organic compound as that which is replaced. Of the former there can be no doubt, while the adoption of the latter as a principle is as yet attended with many difficulties and apparent anomalies, which do not present themselves when we regard these altered compounds after the manner in which our yellow substance is represented in formula 4.

New views all tend to hasten forward science, but a new view is not in itself necessarily an advance. It may often serve as a useful guide-post, when it does not directly help us on our way. Such good results are sure to follow from the discussion of the theory of substitutions, though all the views of its eminent author should not find a permanent place in the science.

I speak with the less confidence in regard to the above formulæ, because I am sensible that the examination of the two compounds described in this paper is by no means complete: a more careful research into the properties and chemical relations, especially of the first of them, would be likely I think to lead to interesting results.

The analyses above given were made as far back as 1838, and in February 1839, and the investigation was left unfinished till I should obtain a fresh supply of the compound. My

\*  $C_{30} \frac{H_{16}}{Cl} O_3 + Cl.$



attention has recently been recalled to the subject by a paper on *Hellenine*, by M. Gerhardt (*Ann. de Chim. et de Phys.* vol. lxxii. p. 163), in which he gives for this substance the formula  $C_{15} H_{10} O_2$  or  $C_{30} H_{20} O_4$ , containing apparently a radical isomeric with the carbo-hydrogen  $C_{30} H_{20}$ , which exists in the iodide above described. By the action of chlorine, hellenine becomes  $(C_{15} H_{10} O_4 + C_{15} H_{10} Cl_4)$  according to Berzelius, or  $(C_{15} H_9 Cl O_2 + H Cl)$  according to Dumas, in which we see a considerable analogy with the formulæ for the oxichloride above described. By the action of anhydrous phosphoric acid on hellenine, a yellow liquid carbo-hydrogen is produced, to which M. Gerhardt gives the name of hellenene, and which is represented by the formula  $C_{15} H_8$ , — the hypothetic radical which enters into the constitution of our oxichloride as it is represented in the formula (4).

These interesting approximations indicate a series of comparative experiments, to which the iodide described in the present paper might be subjected, with the hope of throwing new light on the nature of the ever-varying isomeric modifications, of which the compounds of carbon and hydrogen are susceptible. I hope to be able soon to return to the subject with a view to this investigation.

In regard to the presence of a carbo-hydrogen represented by the formula  $C_{30} H_{20}$  in coal gas, it need not excite our surprise if many other such compounds should hereafter be met with among the volatile and gaseous products obtained from the distillation of coal. When we consider how many less volatile substances of this class have been extracted by Pelletier and Walter\* from the products of the distillation of resin for the manufacture of gas, and how many more volatile ones have been separated by Couerbe† from the gas thus produced when subjected to pressure, we shall be prepared to expect in coal gas also, the vapours of many other volatile substances in addition to those which have hitherto been detected.

I have not as yet proposed any name for the supposed radical  $C_{30} H_{20}$ . It belongs to the same group as mesitylene (Enyl of Berzelius) =  $C_6 H_4$  and retinyle  $C_{18} H_{12}$ , in both of which the elements are in the ratio of 3 to 2. It would be exceedingly desirable to adopt the system of nomenclature proposed by Berzelius for these compounds, in which the name is compounded of the Greek numerals expressive of the number of atoms of each element which are contained in the compound. But that such names may be universally adopted, it is necessary that the same atomic weights should also be

\* Poggendorff's *Annalen*, vol. xlv. p. 81.

† *Ann. de Chim. et de Phys.*, vol. lxix. p. 148.

generally received. In the present case, for example, our green compound would be represented

By  $C_{30}H_{40} + I_2$  according to Berzelius.

By  $C_{60}H_{40} + I_2$  according to Dumas.

And by  $C_{30}H_{20} + I$  according to British chemists.

The compounds of carbon and hydrogen therefore, on the principle of Berzelius, which abstractedly is very valuable as a guide for general nomenclature, would receive in the works of different chemists at least two, and sometimes three different names of foreign origin. Trivial names therefore derived as heretofore from different and various sources, will be likely in the present state of the science to create much less confusion in our rapidly extending, already exceedingly difficult and almost Protean nomenclature.

Durham, May 16, 1840.

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II. *On the Optical Characters of Greenockite (Sulphuret of Cadmium).* By JAMES D. FORBES, Esq., F.R.SS. L. and Ed., Professor of Natural Philosophy in the University of Edinburgh.\*

IT appears from a late number of Professor Jameson's Journal, that the crystallographic characters of this new mineral, as examined by Mr. Brooke, remain ambiguous, and that the crystals sent to him for examination do not enable him positively to say whether it belongs to the rhombohedral or to the prismatic system; it may therefore be interesting to state that I have discovered that it possesses only *one* axis of double refraction in the direction of the axis of the pyramid or prism in which it usually crystallizes, and consequently there can be no doubt that greenockite is a rhombohedral cadmium blende.

Edinburgh, May 18, 1840.

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III. *On a new Species of Biliary Calculus.* By THOMAS TAYLOR, M.R.C.S.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

WHILST engaged in examining the extensive collection of calculi in the museum of the Royal College of Surgeons, which had been entrusted to me for that purpose by the Board of Curators, I remarked, among those in the Hunterian collection, one, which from its extreme lightness and peculiar

\* Communicated by the Author. We were favoured with this article in the middle of May, but from an oversight which we regret its insertion was omitted.