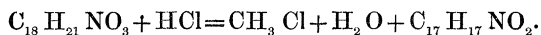


identical with those of the above-mentioned previous researches; and he claims the following results as new:—The conditions as to transfer and transformation of heat which must be fulfilled in order that permanence of type may be realized, exactly or approximately, in a wave of finite longitudinal disturbance in any elastic medium; the types of wave which enable such conditions to be fulfilled with a given law of the conduction of heat; the velocity of advance of such waves; and some special results as to the rate of change of type in adiabatic waves. He also claims as new the method of investigation by the aid of *mass-velocity* and *mass-coordinates*, which he alleges to possess great advantages in point of simplicity.

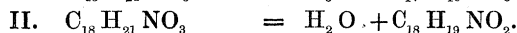
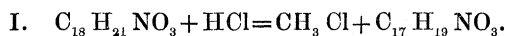
IV. “Researches into the Constitution of the Opium Bases.—Part III. On the Action of Hydrochloric Acid on Codeia.” By AUGUSTUS MATHIESSEN, F.R.S., Lecturer on Chemistry in St. Bartholomew’s Hospital, and C. R. A. WRIGHT, B.Sc. Received July 23, 1869.

§ 1. *On the Action of Hydrochloric Acid on Codeia.*

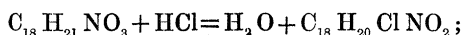
In Part II. (Proc. Roy. Soc. vol. xvii. p. 460) it was shown that when codeia is heated with excess of hydrochloric acid under pressure that it splits up into chloride of methyl, water, and apomorpha, thus—



At the time it appeared probable that one of the two following reactions would first take place, forming an intermediate product:—



On investigation, however, it has been found that neither the one nor the other takes place, at least as the chief reaction; for by heating codeia with excess of hydrochloric acid on the water-bath, a body is obtained by the following reaction—



and this base, when heated under pressure with hydrochloric acid, splits up into chloride of methyl and apomorpha,



The new base may be obtained in a state of purity thus:—codeia is heated under paraffin on the water-bath with ten to fifteen times its weight of strong hydrochloric acid for twelve to fifteen hours, and the resulting brownish liquid evaporated to dryness on the water-bath; the residue is dissolved in water, and excess of bicarbonate of sodium added, whereby a voluminous white precipitate is formed, consisting chiefly of the new base mixed with a trace of apomorpha. The filtrate contains the unaltered

codeia mixed with a little of the new base, which is not quite insoluble in bicarbonate of sodium solution; the precipitate is washed with ammonia-water to remove the trace of apomorphia (which is much more soluble in ammonia than the new base), and is then dissolved in hydrochloric acid and fractionally precipitated by bicarbonate of sodium: the second fraction is pure white, and is free from apomorphia and codeia; this is then extracted with ether, which dissolves almost the whole. The clear ethereal solution is then shaken up with a few drops of hydrochloric acid, and the solution of hydrochlorate thus obtained, if coloured, must be fractionally precipitated by bicarbonate of sodium, and the ether and hydrochloric-acid process repeated; the resulting product is a viscid colourless solution of the hydrochlorate of the new base, which refuses to crystallize. When evaporated on the water-bath, the dry residue yielded the following numbers on analysis:—

(I.) 0·3270 gramme, burnt with lead chromate, gave 0·7230 carbonic acid and 0·1820 water.

(II.) 0·3080 gramme gave 0·6870 carbonic acid and 0·1720 water.

(III) 0·3010 gramme, burnt with lime, gave 0·2450 silver chloride.

	Calculated.		I.	Found. II.	III.
C ₁₈	216	61·01	60·30	60·83	
H ₂₁	21	5·93	6·18	6·20	
Cl ₂	71	20·04			20·14
N	14	3·95			
O ₂	32	9·07			
C ₁₈ H ₂₀ ClNO ₂ , HCl	354	100·00			

The hydrochlorate, when fractionally precipitated by bicarbonate of sodium, yielded the base as a snow-white mass, scarcely affected by exposure to air, very soluble in alcohol and ether, but not crystallizable from those menstrua owing to decomposition; when well washed and dried, first over sulphuric acid and then at about 60°, it gave the following results on analysis:—

(I.) 0·3380 gramme gave 0·8410 carbonic acid and 0·1900 water.

(II.) 0·2680 gramme, burnt with lime, gave 0·1160 silver chloride.

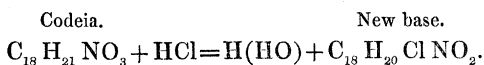
	Calculated.		I.	Found. II.
C ₁₈	216	68·03	67·87	
H ₂₀	20	6·29	6·25	
Cl	35·5	11·18		10·71
N	14	4·41		
O ₂	32	10·09		
C ₁₈ H ₂₀ ClNO ₂	317·5	100·00		

Another portion of hydrochlorate converted into platinum-salt gave a

yellow precipitate permanent in the air, but decomposed when heated to 100° in a moist state; dried several days over sulphuric acid, 0·5380 gramme gave 0·1000 metallic platinum.

	per cent.
Found	18·60
The formula $(C_{18}H_{20}ClNO_2, HCl)_2 PtCl_4$ requires	18·81
The codeia salt requiring	19·50

From these numbers it appears that the new base is formed from codeia by the replacement of an atom of hydroxyl by one of chlorine, thus—



If codeia be regarded as being formed on the mixed type $\begin{smallmatrix} H_3N \\ H_2O \end{smallmatrix}$, then the new base may be looked upon as formed on the mixed type $\begin{smallmatrix} H_3N \\ HCl \end{smallmatrix}$; and, using Professor Foster's nomenclature* for these types (viz. oxynitride and chloronitride respectively), codeia would be oxycodide, and the new base chlorocodide; but until further investigation affords some knowledge of the nature of the radicals occurring in codeia and morphia, it would be premature to attempt to give rational formulæ for these bases.

The following Table (p. 86) exhibits the comparative reactions of solutions containing 1 per cent. of the hydrochlorates of morphia, codeia, apomorphia, and chlorocodide respectively.

The physiological action of chlorocodide appears to be much less marked than that of apomorphia. Doses of $\frac{1}{4}$ grain of the hydrochlorate taken internally and $\frac{1}{10}$ grain injected subcutaneously produced no appreciable effect; Dr. Gee is now engaged in studying this subject.

§ 2. *Action of Hydrochloric Acid on Chlorocodide.*

When the hydrochlorate of this base is sealed up with eight to fifteen times its weight of strong hydrochloric acid and heated to 140°–150° for three hours, the tube is found, after cooling, to contain a layer of liquid chloride of methyl floating at the top: the tarry contents of the tube, when dissolved in water and precipitated by bicarbonate of sodium, yield, on shaking up the ethereal extract with a few drops of hydrochloric acid, a copious supply of crystals of hydrochlorate of apomorphia; these, when drained from the mother liquors, washed with cold water, and recrystallized, had all the physical properties of the hydrochlorate of apomorphia from morphia, gave the same qualitative reactions, and produced the same physiological effects, and gave the following numbers on analysis after drying at 100°:—

(I.) 0·3090 gramme, burnt with lead chromate, gave 0·7595 carbonic acid and 0·1740 water.

(II.) 0·4030 gramme, burnt with lime, gave 0·1910 silver chloride.

* Watts's Dictionary, vol. iv. p. 124.

	Ferrie Chloride.	Nitric Acid.	Sulphuric Acid and Bichromate of Potassium.	Bleaching-powder Solution and a drop of Hydrochloric Acid.	Corrosive Sublimated Solution.	Nitrate of Silver.
Morphia	Greenish-blue coloration. Morphia alone yields a pure blue.	Yellow coloration.	—	—	Stronger solutions give a white precipitate soluble on boiling, crystallizing out on cooling.	Slowly reduced.
Codeia	—	Yellowish coloration.	—	—	Same as morphia.	Scarcely any reduction
Apomorphia..	Dark purple amethyst coloration.	Dark blood-red colour.	Dark blood-red colour.	Dark blood-red colour.	White precipitate decomposed on boiling with blood-red coloration.	Reduced more quickly than the morphia.
Chlorocodide..	Pale amethyst coloration.	Pale red colour.	Evanescant pale red coloration.	Pale red colour.	White precipitate decomposed on boiling with pale red colour.	Same as apomorphia.
	Caustic Potash.	Carbonate of Sodium.	Ammonia.	Iodide of Potassium.	Oxalate of Ammonium.	Phosphate of Sodium.
Morphia	Stronger solutions give a white precipitate scarcely soluble in excess.	Stronger solutions give a white precipitate insoluble in excess.	—	—	—	—
Codeia	Stronger solutions give a white precipitate scarcely soluble in excess.	Very strong solutions cause codeia to crystallize out slowly after some hours.	—	—	—	—
Apomorphia..	White precipitate readily soluble in excess; solution soon decomposes.	White precipitate slightly soluble in excess.	White precipitate soluble in excess; solution soon decomposing.	White precipitate.	White precipitate.	White precipitate.
Chlorocodide	White precipitate difficultly soluble in excess.	White precipitate slightly soluble in excess.	White precipitate slightly soluble in excess.	White precipitate.	—	White precipitate.

	Calculated.		Found.	
			I.	II.
C ₁₇	204	67·22	67·04	
H ₁₈	18	5·93	6·25	
N	14	4·61		
O ₂	32	10·54		
Cl	35·5	11·70		11·72
C ₁₇ H ₁₇ NO ₂ , HCl	303·5	100·00		

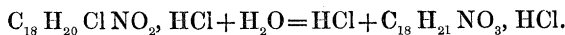
Hence the reaction which takes place is



It is worthy of notice that this reaction probably takes place gradually, while that whereby apomorphia and chloride of methyl are formed direct from codeia appears to occur suddenly, thereby bursting the large majority of sealed tubes used: this never occurred with chlorocodide.

§ 3. *Action of Water on the Hydrochlorate of Chlorocodide.*

When the hydrochlorate (obtained by dissolving the base freed from codeia &c. by the process previously described in as small an excess of hydrochloric acid as possible) is sealed up with ten to fifteen times its weight of water and heated for three hours to 130°–140°, it splits up into hydrochloric acid and hydrochlorate of codeia, no gas whatever being formed during the reaction.



In two experiments the amount of free hydrochloric acid thus formed was estimated by titration with a solution of carbonate of sodium, and after subtraction of the small amount due to the excess of hydrochloric acid in the original liquid (estimated in the same way), was found to amount respectively to 9 and 10 per cent. of the hydrochlorate employed, the theoretical amount according to the above equation being 10·3; the amount of undecomposed chlorocodide was found to be very small, the liquid resulting from the digestion giving but a minute precipitate with carbonate of sodium. The filtrate from the carbonate-of-sodium precipitate was extracted with ether, and the ethereal solution obtained shaken with a few drops of hydrochloric acid; an oily liquid was thus obtained, which on standing several hours deposited crystals; these, when drained from the mother liquors and recrystallized, had the character of hydrochlorate of codeia, and gave the following numbers after drying in an ordinary water-bath till constant in weight.

As crystallized hydrochlorate of codeia is stated to lose one-fourth of its water of crystallization at 100°, a sample was prepared by dissolving codeia in hydrochloric acid and recrystallizing the product; after drying in the same water-bath it was also burnt as a comparison (III.).

(I.) 0·3110 gramme of hydrochlorate of codeia from chlorocodide gave 0·6595 carbonic acid and 0·2015 water.

(II.) 0·2790 gramme of the same, burnt with lime, gave 0·1090 silver chloride.

(III.) 0·3460 gramme of hydrochlorate of codeia made from codeia gave 0·7360 carbonic acid and 0·2300 water.

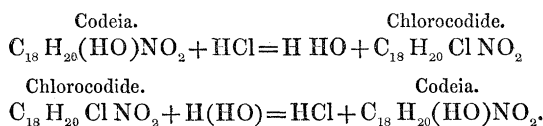
	Calculated.		Found.		
			I.	II.	III.
C ₁₈	216	58·13	57·83		58·01
H ₂₆	26	7·00	7·20		7·38
O ₅	80	21·54			
N	14	3·77			
Cl	35·5	9·56		9·67	
C ₁₈ H ₂₁ NO ₃ , HCl + 2 H ₂ O	371·5	100·00			

A portion of the regenerated hydrochlorate of codeia was precipitated by caustic potash and crystallized from benzole; after drying at 120° it yielded these numbers.

0·3325 gramme, burnt with oxide of copper and oxygen, gave 0·8795 carbonic acid and 0·2185 water.

	Calculated.		Found.
C ₁₈	216	72·24	72·14
H ₂₁	21	7·02	7·30
N	14	4·68	
O ₃	48	16·06	
C ₁₈ H ₂₁ NO ₃	299	100·00	

The influence of mass upon chemical reactions is well illustrated by the inverse reactions taking place between codeia and hydrochloric acid in excess, and chlorocodide with water in excess.



The codeia employed in the foregoing experiments forms part of a second supply kindly given to us by Messrs. M'Farlane of Edinburgh.

§ 4. On the Crystalline Form of Chloride of Apomorpha.

By Prof. W. H. MILLER, For. Sec. R.S.

Prof. Miller has kindly determined the crystalline form of the chloride of apomorpha, which we here annex.

Chloride of apomorpha.

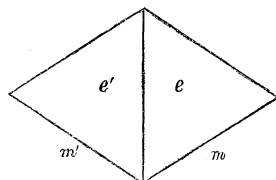
Prismatic:—

$$001, 101 = 29^\circ 26' \cdot 5; 100, 110 = 56^\circ 48' \cdot 5.$$

Simple forms:—*e*, 101 : *m*, 110.

Angles between normals to the faces:—

$$\begin{array}{ll} e \ e' \dots 58^\circ 53' \\ m \ m' \dots 66 \ 23 \\ e \ m \dots 74 \ 23 \end{array}$$



No cleavage observable.

The crystals are small, the length and breadth of one of the largest being 0·9 and 0·22 millimetres respectively.