

**Contributions towards the history of caproic and œnanthylic acids / by J.S. Brazier and G. Gossleth.**

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# CONTRIBUTIONS

TOWARDS

## THE HISTORY OF CAPROIC AND CENANTHYLIC ACIDS.

[READ BEFORE THE CHEMICAL SOCIETY OF LONDON.]

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THE leading notions, which begin to elucidate the vast number of observations collected in the department of organic chemistry, have been acquired in the careful study of a comparatively limited number of groups of analogous substances. The investigation of a series of bodies closely allied to each other in their composition and properties, and a comparison of their composition and properties, imparted to the results obtained a degree of interest, which could not have been possibly claimed by the most accurate and minute examination of an isolated compound.

Among the groups of substances, the study of which has thus most materially assisted in the elaboration of our theoretical views, the series of acids, usually called fatty acids, appears in the first rank. This series, commencing with formic acid, the simplest of all organic acids, and terminating with an acid of so high an equivalent as melissic acid, discovered by Mr. Brodie, is at once distinguished by the definite character of its members, by the extent to which it is represented by well-investigated terms, and by the variety of sources, belonging to almost all the various departments of organic chemistry from which these terms have been derived. Descending from the alcohols by way of the aldehydes, and connected with the former group in another manner by the nitriles, again related in its derivatives with marsh-gas and its homologues, as well as with the increasing family of acetones, the history of this group, when traced in its various ramifications, extends over a field on which we meet with almost all the compounds essentially concerned in the progress of chemical science.



In the following pages, we beg to communicate to the Society, a few contributions towards the history of the fatty acids, which, notwithstanding their fragmentary nature, may be acceptable on account of the interest attached to the subject. These communications refer to the sixth and seventh term of the series of fatty acids, namely caproic and cœnanthylic acids.

#### CAPROIC ACID.

This acid, discovered by Chevreul in the course of his unforgotten researches into the nature of fatty bodies, and subsequently met with in cocoa-nut oil by Fehling,\* has been produced of late under very remarkable circumstances from cyanide of amyl, by Messrs. Kolbe and Frankland.† In order to avoid the tedious processes of saponification, and subsequent fractional distillation of the volatile products, or of separating the acids by the different solubility of their baryta-salts, we resolved to prepare the acid by the latter method. In the course of this process, we made one or two observations which may be mentioned.

The sulphamylate of potassa, used in making cyanide of amyl, was prepared at once from sulphamylic acid, by saturating it with crude carbonate of potassa. Nearly the whole of the excess of sulphate of potassa formed was separated during this operation, the remaining portion crystallizing out by the evaporation of the solution.

The perfectly dry sulphamylate of potassa, when distilled with cyanide of potassium in the proportion of three to one, yields cyanide of amyl. In the commencement we performed this distillation on a rather considerable scale in iron retorts: the irregular action of the heat, however, induced the formation of a large amount of secondary products; and we found it more advisable to work with smaller portions. The operation succeeds very well in Florence flasks, placed obliquely upon a wire-gauze over a gas-burner. The liquid obtained in this distillation is by no means a definite compound. Its terrible odour indicates at once the presence of a considerable amount of prussic acid. When subjected to distillation, it begins to boil at about 125° C. (257° F.), the boiling-point rising gradually to 150° C. (302° F.), about which temperature, a semi-solid, yellowish-white mass, of crystalline appearance, remains behind in the retort. A similar product is deposited in the tube of the condenser. It may here at once be stated that this liquid contains, in addition to cyanide of amyl, a good deal of fusel-oil, and moreover a considerable quantity of both liquid cyanate and solid cyanurate of amyl, the two latter evidently arising from the presence of a large amount of cyanate of potassa in

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\* Ann. Ch. Pharm. LIII., 390.

† Ann. Ch. Pharm. LXIX., 418.



the commercial cyanide of potassium. This substance, which is now manufactured in this country by hundredweights, is invariably prepared by Liebig's process, the success of which, as is well known, actually depends upon the simultaneous formation of the cyanate.

In the first place, we attempted to purify the crude cyanide previously to its conversion into caproic acid; but after having ascertained the nature of the impurities, we at once subjected the crude product collected between  $130^{\circ}$  and  $150^{\circ}$  to the action of the alkali. The products of decomposition furnished by the cyanide and cyanate are so opposite in their chemical character—the one yielding a strong acid, caproic acid, the other a powerful base, amylamine or valeramine, while the fusel-oil present remains unaltered—that the separation, after decomposition follows as a matter of course, whilst separation by fractional distillation before the action, would have been a tedious and nevertheless imperfect operation.

The conversion of the cyanide of amyl may be effected by an aqueous solution of potassa: we found, however, that the operation succeeds much better with a solution of the alkali in alcohol. The mixture, when boiled in a flask connected with a condenser in such a manner as to induce the liquid to return to the alkali, readily changes into a pasty mass, while torrents of ammonia are evolved. After half an hour's ebullition, the mixture is introduced into a retort and subjected to distillation, when a small quantity of ammonia, alcohol, amylamine, and fusel-oil distil over, a solution of caproate of potassa remaining behind, which usually solidifies on cooling into a semi-crystalline mass.

The distillate was mixed with some hydrochloric acid, and subjected once more to distillation; it began to boil at about  $78^{\circ}$  C. ( $172^{\circ}4$  F.), the first product consisting of alcohol; the boiling-point rose gradually to  $131^{\circ}$  C. ( $267^{\circ}8$  F.), at which temperature pure fusel-oil distilled over, a syrupy mass remaining behind, containing chiefly hydrochlorate of amylamine, and from which an additional quantity of fusel-oil was separated by addition of water. The dilute solution, when boiled for some time, in order to drive off fusel-oil, which was still mechanically adhering, and distilled with potassa, yielded a considerable quantity of pure amylamine. The production of this base under these circumstances is, as we have mentioned, due to the decomposition of the cyanate and cyanurate of amyl: these substances as Wurtz has shown, assimilating the elements of water, are split up into carbonic acid and amylamine. In several operations, the production of the latter base nearly equalled the quantity of caproic acid obtained, which shows how much cyanate is present in many kinds of commercial cyanide of potassium. With respect to the properties of amylamine, we have scarcely to add anything to Wurtz's description; however, as we had a considerable quantity of the substance at our disposal, we determined its boiling-point with accuracy.

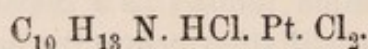


Amylamine boils constantly at  $93^{\circ}$  C. ( $199^{\circ}4$  F.) We adduce, moreover, an analysis of the platinum-salt of this base, which leaves no doubt as to its identity with amylamine.

The platinum-salt, being soluble in water, was easily purified by one or two recrystallizations.

- I. 0.5722 grms. of platinum-salt gave :  
 0.4259     "     carbonic acid, and  
 0.2578     "     water.  
 II. 0.6210     "     platinum-salt gave :  
 0.2077     "     platinum.

These numbers lead to the following per centage, which we place in juxtaposition with the theoretical values of the formula,



				Theory.	Experiment.
10 eqs. of Carbon	-	-	60.00	20.46	20.30
14     "     Hydrogen	-	-	14.00	4.78	5.00
1     "     Nitrogen	-	-	14.00	4.78	—
3     "     Chlorine	-	-	106.50	36.33	—
1     "     Platinum	-	-	98.68	33.65	33.45
1 eq. of Bichloride of Platinum and Amylamine				293.18    100.00	—

The solution of caproate of potassa, concentrated if requisite by evaporation, was gradually mixed with sulphuric acid, when caproic acid separated as an oily liquid, lighter than water. It was removed by a tap-funnel, and subjected to rectification.

The acid obtained in this manner was not perfectly pure; when submitted to distillation, it was found that the thermometer rose at once to, and became constant at,  $198^{\circ}$  C. ( $388^{\circ}4$  F.); at which temperature, the larger portion of the fluid distilled over; the mercury then rose gradually to  $211^{\circ}$  C. ( $411^{\circ}8$  F.) The first fraction, when rectified, exhibited exactly the same boiling-point as before, several ounces distilling over without any oscillation of the mercury, whence we do not hesitate to consider  $198^{\circ}$  C. ( $388^{\circ}4$  F.) as the boiling-point of caproic acid: Fehling\* had found that the acid obtained from cocoa-nut oil boiled at  $202^{\circ}$  C. ( $395^{\circ}6$  F.).

#### CAPROATE OF AMYL.

We have just stated that the thermometer continued to rise after the distillation of the pure acid. The product passing over between  $200^{\circ}$  and  $211^{\circ}$ , differed in its odour from that of caproic acid; it was found

\* Ann. Ch. Pharm. LIH. 390.



to be partly soluble in alkaline, and not at all in acid liquids, and formed only a comparatively small per centage of the total amount of liquid. In order to obtain a sufficient quantity of this compound for examination, a considerable portion of crude caproic acid was treated with a solution of carbonate of potassa, when the caproic acid was dissolved with evolution of carbonic acid, an oily liquid separating on the surface of the solution. When removed with a separating funnel and dried over chloride of calcium, it exhibited after rectification, a constant boiling-point at  $211^{\circ}$  C. ( $411^{\circ}8$  F.).

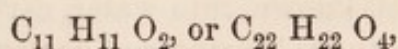
The analysis of the oily liquid gave the following results:

I. 0.2485 grms. of substance gave :			
0.6410	„	carbonic acid, and	
0.2675	„	water.	
II. 0.2075 „ substance gave :			
0.5386	„	carbonic acid, and	
0.2231	„	water.	

Percentage-composition :

		I.	II.
Carbon	- -	70.75	70.80
Hydrogen	- -	11.95	11.94

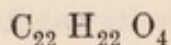
These numbers closely agree with the formula,



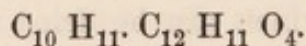
as exhibited in the following comparison of the theoretical values with the results of experiment:

				Theory.	Mean of Experiment
22 eqs. of Carbon	-	-	132	70.96	70.78
22 „ Hydrogen	-	-	22	11.82	11.94
4 „ Oxygen	-	-	32	17.22	—
				186	100.00

The formula,



represents the composition of caproate of amyl:



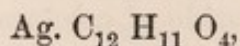
The observed boiling-point of this compound coincides pretty closely with the number calculated, if we start from the boiling-point of valerate of amyl, which, according to Balard's determination, is  $190^{\circ}$  C. ( $374^{\circ}$  F.) The deportment of the above substance with an alcoholic solution of potassa, leaves no doubt in this respect. The mixture, when heated, was readily converted into a gelatinous mass, from which water separated pure fusel-oil, while addition of sulphuric acid to the remaining alkaline solution, induced the liberation of



an oily acid, which by analysis was proved to be caproic acid. When it was separated by distillation, dissolved in ammonia and converted into a silver-salt

0.2814 grms. of silver-salt gave:  
 0.1408 „ silver = 48.65 per cent. of silver.

The formula,



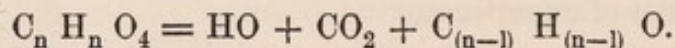
requires 48.43 per cent.

Caproate of amyl has a very disagreeable smell and pungent taste, is perfectly insoluble in water, of a lower specific gravity, but soluble in every proportion of alcohol and ether.

The formation of caproate of amyl under the adduced circumstances, appeared at the first glance rather enigmatical. We soon found, however, that fusel-oil is soluble to a certain extent in a solution of caproate of potassa. The separation of caproic acid by sulphuric acid in the presence of amyl-alcohol could not fail to produce a certain quantity of the compound ether in question.

#### ACTION OF HEAT UPON CAPROATE OF BARYTA.

The members of the series  $\text{C}_n \text{H}_n \text{O}_4$ , when subjected to the action of heat, split, as is well known, into water, carbonic acid, and a new class of bodies known under the name of acetones or ketones, according to the following equation:—



This metamorphosis is generally effected by the distillation of the lime- or baryta-salts, in which case the carbon becomes fixed in the form of carbonate.

In preparing the ketone of caproic acid, we availed ourselves of the baryta-salt.

This salt is easily prepared by means of carbonate of baryta and caproic acid; it is very soluble in water. The solution, when left to evaporate *in vacuo* over sulphuric acid, deposits crystalline plates. By ebullition, the odour of caproic acid becomes perceptible, and a white mass separates, which can be dried without decomposition at a temperature a little above 100° C. The dry mass evidently a somewhat basic salt, is brittle and may be easily powdered; for the distillation of the salt we employed small quantities at a time. At a gentle heat, the salt fuses without charring in the least, nearly white carbonate of baryta remaining behind; nevertheless, only a comparatively small quantity of liquid product is obtained as distillate. Experiment showed at once that the action by no means consists exclusively in a separation of carbonic acid; for during the whole process a permanent inflammable gas was evolved, the quantity of



which appeared to increase in some measure with the temperature at which the distillation was performed. Caproate of baryta, when suddenly exposed to a rapidly rising temperature, disengages this gas in considerable quantities, only a small portion of oily products being formed, which are moreover very dark and resinous, whilst the distillate obtained by moderate temperatures is nearly colourless. The carbonate of baryta which remains in the retort is nearly black from separated carbon. These facts, as well as the observations made by Chancel and Guckelberger\* in the analogous decomposition of butyric, valeric, and caprylic acids, left no doubt that the liquid product was a mixture of various substances. When dried over chloride of calcium and subjected to distillation, it commenced boiling at  $120^{\circ}$  C. ( $248^{\circ}$  F.), the boiling-point rising gradually to  $170^{\circ}$  C. ( $338^{\circ}$  F.). Between  $160^{\circ}$  and  $170^{\circ}$  the largest quantity was collected. This portion, on rectification, showed a pretty constant boiling-point at  $165^{\circ}$  C. ( $329^{\circ}$  F.). With the lower portions, no constant boiling-temperature could be observed. Several combustions made with this product, exhibited invariably a deficiency of carbon when compared with the percentage of carbon required by the formula of caprone,  $C_{11}H_{11}O$ . This, as well as the results of Chancel, who actually separated butyrale, or at all events a substance of similar composition from the product of distillation of butyrate of lime, lead us to believe that a small quantity of caprale,  $C_{12}H_{12}O_2$ , may be formed in this process.

This assumption is supported by the deportment of the lower distillate, from which ammonia removes a small portion of matter. The ammoniacal solution, after having been exposed to the air for some time, yields with acids oily globules having the characteristics of caproic acid. Unfortunately, we had not enough material to elaborate this question any further. We were, however, benefitted by the observation, inasmuch as it induced us to submit the chief fraction boiling at about  $165^{\circ}$ , previously to analysis, to an additional distillation over hydrate of potassa. After this treatment, it showed a constant-boiling point at  $165^{\circ}$  C. ( $329^{\circ}$  F.). When burnt with protoxide of copper, this liquid gave the following results :

- |     |        |       |                      |
|-----|--------|-------|----------------------|
| I.  | 0.1641 | grms. | of substance gave :  |
|     | 0.4655 | ”     | ” carbonic acid, and |
|     | 0.1949 | ”     | ” water.             |
| II. | 0.2263 | ”     | ” substance gave :   |
|     | 0.6423 | ”     | ” carbonic acid, and |
|     | 0.2668 | ”     | ” water.             |

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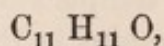
\* Ann. Ch. Pharm. LXIX. 20.



## Percentage-composition :

	I.	II.
Carbon - - -	77.36	77.42
Hydrogen - - -	13.18	13.10

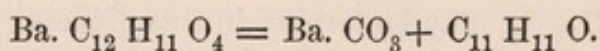
These numbers closely correspond with the formula



as may be seen from the following table :

	Theory.	Mean of Experiment.
11 eqs. of Carbon - - -	66    77.64	77.39
11    „    Hydrogen - - -	11    12.94	13.14
1    „    Oxygen - - -	8    9.42	—
1 eq. of Caprone - - -	85    100.00	

Caprone is a very mobile liquid, insoluble in water, to which, however, it imparts its peculiar odour ; it is readily soluble in alcohol and ether. After being distilled from potassa, it is perfectly colourless, but rapidly turns brown when in contact with the atmosphere, probably in consequence of oxidation. Its boiling-point is  $165^{\circ}$ , C. ( $329^{\circ}$  F.), and its specific gravity is lower than that of water. These results show that one phase of the action of heat upon caproate of baryta, may be represented by the equation :



We say one phase, because a series of other metamorphoses is proceeding simultaneously with the conversion of a portion of the acid into caprone. The amount of this substance obtained is quite out of proportion with the quantity of baryta-salt employed. We have mentioned that we have reason to believe that the aldehyde of caproic acid is simultaneously formed, and alluded to the large quantity of permanent gas disengaged. This gas consists chiefly of hydrocarbons, and probably contains a similar mixture of the hydrocarbons  $C_n H_n$ , which Dr. Hofmann observed in the distillation of valerianic acid.\*

The preparation of caprone adds another member to the group of ketones running parallel with the series of fatty acids. This group, first announced in the formation of acetone, which may be still considered as its prototype, and subsequently illustrated by Chancel's researches into the derivatives of butyric and valeric acids, embraces

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\* The chief component of this gas is, as Dr. Hofmann has stated, propylene. He has since learnt from M. Cahours, that pelargonic, caprylic, and cœnanthylic acids likewise yield this hydrocarbon in preponderating quantities, so that we may fairly assume that caproic acid exhibits a similar deportment.



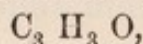
at this moment the following members, which we give in juxtaposition with their mother acids :

Acetic acid	-	$C_4 H_4 O_4 ; C_3 H_3 O,$	Acetone;	Liebig & Dumas.
Propionic acid	}	$C_6 H_6 O_4 ; C_5 H_5 O,$	{ Propione; Metacetone;	Frémy.
Metacetic acid				
Butyric acid	-	$C_8 H_8 O_4 ; C_7 H_7 O,$	Butyrone;	Chancel.
Valeric acid	-	$C_{10} H_{10} O_4 ; C_9 H_9 O,$	Valerone;	Chancel.
Caproic acid	-	$C_{12} H_{12} O_4 ; C_{11} H_{11} O,$	Caprone;	B. & G.
Caprylic acid	-	$C_{16} H_{16} O_4 ; C_{15} H_{15} O,$	Caprylone;	Guckel-berger.
Margaric acid	-	$C_{34} H_{34} O_4 ; C_{33} H_{33} O,$	Margarone;	Bussy.

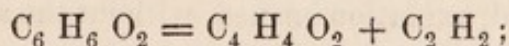
This table shows that the ketone of formic acid is still wanting; the series then regularly ascends up to cenanthylic acid, whose derivative has not yet been prepared; we perceive, moreover, that a wide gap occurs between caprylic and margaric acid, the filling up of which will require some time and labour. It deserves to be mentioned that one of the terms which we have inserted in the above table, has not hitherto been obtained from the collateral acid. Propione (metacetone) originally prepared by Frémy by distilling sugar, starch, or gum, with lime, has been represented by its discoverer by the formula  $C_6 H_5 O$ ; it is probable, however, that Frémy's substance contains one equiv. of carbon less.\* Its properties coincide in almost every respect with propione, as pointed out by theory.

Acetone and its congeners have been of late the subject of some interesting speculations on the part of M. Chancel.† The formula which we have given in the above table, represents 2 volumes of vapour, and this is the mode of condensation adopted by the majority of chemists. M. Chancel on the other hand is of opinion, that the ketones, like the hydrocarbons, contain 4 vols. of vapour: he doubles the formulæ, and considers these substances as formed by the intimate combination of 1 equivalent of the aldehyde of the acid with 1 equivalent of the hydrocarbon belonging to the group which is placed a step lower on the ladder of organic substances.

According to this view, acetone is not represented by



but by



i.e., it has to be considered as a combination of the aldehyde (*par ex-*

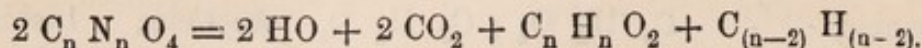
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\* Since the above was written, the formation of propione from propionic acid has been made the subject of investigation by Mr. Morley. He assigns to it the formula we have given above, namely,  $C_5 H_5 O$ .—(Chem. Soc. Qu. J. iv. 1.)

† J. Pharm. [3] XIII. 468.



*cellence*), and methylene: consequently the ketones would always arise from the decomposition of 2 eqs. of the respective acids:



The following table, into which we introduce the boiling-points which have been observed, exhibits the various ketones when viewed in this light:

						Boiling-point.
Acetone	-	$C_6 H_6 O_2$	=	$C_4 H_4 O_2$	+ $C_2 H_2$ ...	56° C. (132°·8 F.)
Propione	-	$C_{10} H_{10} O_2$	=	$C_6 H_6 O_2$	+ $C_4 H_4$ ...	84° C. (183°·2 F.)
Butyrone	-	$C_{14} H_{14} O_2$	=	$C_8 H_8 O_2$	+ $C_6 H_6$ ...	144° C. (291°·2 F.)
Valerone	-	$C_{18} H_{18} O_2$	=	$C_{10} H_{10} O_2$	+ $C_8 H_8$	
Caprone	-	$C_{22} H_{22} O_2$	=	$C_{12} H_{12} O_2$	+ $C_{10} H_{10}$ ...	165° C. (329°·0 F.)
Caprylone	-	$C_{30} H_{30} O_2$	=	$C_{16} H_{16} O_2$	+ $C_{14} H_{14}$ ...	178° C. (352°·4 F.)
Margarone	-	$C_{66} H_{66} O_2$	=	$C_{34} H_{34} O_2$	+ $C_{32} H_{32}$	

Chancel's view is chiefly supported by the deportment of some of the ketones under the influence of oxidizing agents. In fact, acetone when boiled with chromic acid yields a mixture of acetic and formic acids, the former being (in the conception of this theory) derived from the aldehyde, while the latter is due to the presence of a term belonging to the lower series. If acetone were  $C_3 H_3 O$ , this conversion would be almost unintelligible. In the same manner, propione is converted into propionic and acetic acids. By treating butyrone with nitric acid, Chancel\* obtains nitropropionic acid, which may have been formed by the oxidation of the propylene; Chancel gives no account of what becomes of the other term, the butaldehyde occurring in his formula. On the other hand, we find that the formation of butyrone is invariably attended by a simultaneous production of butaldehyde (butyrale), which may be due to a partial decomposition of the butyrone in the nascent state, probably with evolution of propylene. The generation of valerone, and, as we have seen, of caprone, gives rise to similar phenomena. It remained now to study the deportment of the latter compound under the influence of oxidizing agents.

#### ACTION OF NITRIC ACID UPON CAPRONE.

This body was very readily attacked by nitric acid. If strong acid was employed, oxidation ensued, without the application of heat: as soon as the evolution of nitrous fumes had ceased, the liquid in the retort was saturated with carbonate of potassa, when an oily liquid of a peculiar aromatic odour separated, which was insoluble in an excess of the alkaline liquid. The quantity at our disposal was so very

\* J. Pharm. [3] XIII. 463.



small, as to preclude altogether the possibility of a closer examination.

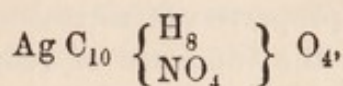
The alkaline solution separated from the oil by ebullition was now acidified with sulphuric acid, and subjected to distillation, when an acid liquid was obtained upon which a small quantity of an acid oil was floating. When saturated with ammonia and precipitated with nitrate of silver, a white crystalline silver-salt was obtained. The quantity of material at our disposal was just sufficient for a silver-determination.

0.4566 grms. of silver-salt gave:

0.1088 „ silver.

Percentage of silver 42.24.

This number, although somewhat low, would indicate that the salt analysed was nitrovalerate of silver; the slight deflagration which occurred on igniting the salt, gives further evidence in favour of this view. The formula,



requires 42.5 of silver.

If the acid formed by the action of nitric acid upon caprone be actually nitrovaleric acid—which has to be proved by additional experimental evidence—the deportment of this ketone would be perfectly analogous to that of butyrone, which yields nitropropionic acid. In both cases, we may ask what becomes of the aldehydes, which, according to the analogy of the lower terms, should be converted into their correlative acids, namely into caproic and butyric acids. These acids which, according to Chancel's formula, should be formed in quantities equal to those of nitrovaleric and nitropropionic acid, and which should be produced even more readily than the latter acids, have not as yet been observed in the respective processes. Hence it appears that many further researches are requisite in order to establish Chancel's interesting speculations. The chief difficulty which we meet in the study of the higher terms of this series, is the great amount of acid required, the preparation of which is both laborious and expensive.

Before leaving this question, we may still take a glance at the boiling-point of the substance under consideration. The difference of the boiling-point of acetone and butyrone  $144^\circ - 56^\circ = 88 = 4 \times 22$ , agrees very well with Chancel's view; the boiling-point of propione is stated at  $84^\circ$  instead of  $100^\circ$ , which would be the temperature assigned by theory. However, as propione has never been prepared from propionic acid, we can scarcely place implicit reliance upon the statements at present in our possession; it is possible that the product investigated, produced as it was in an irregular process of de-



structive distillation, still contained some of the substances simultaneously generated, acetone, &c.\*

The boiling-points of caprone and caprylone (Guckelberger) are not at all favourable to Chancel's assumption. Caprone boiling at  $165^{\circ}\text{C}$ . ( $329^{\circ}\text{F}$ .), should, according to theory, boil as high as  $232^{\circ}\text{C}$ . ( $499^{\circ}\text{F}$ .); caprylone, the theoretical boiling-point of which is  $320^{\circ}$ , has been found to enter into ebullition at as low a temperature as  $178^{\circ}\text{C}$ . ( $352^{\circ}\text{F}$ .). We have, however, to bear in mind that the present state of our knowledge respecting boiling-points is very deficient; the empirical rule at which we have arrived holds good only for a certain range of the thermometer, the difference of the boiling-temperatures increasing towards the lower and decreasing towards the upper limit.

We have to apologise for the unsatisfactory state in which we are obliged to leave this question for the present: we say for the present, because it is our intention to return to this subject as soon as possible. We hope more especially soon to obtain additional data respecting the composition and the properties of nitrovaleric acid. The deportment of this acid under the influence of reducing agents promises interesting results; for should this acid—as we have every reason to believe—imitate the behaviour of nitrobenzoic acid,† its analogue in the benzoyl-series, it will put us in possession of carbobutylic acid, from which a single step downward would lead to butylamine.

#### DECOMPOSITION OF CAPROIC ACID UNDER THE INFLUENCE OF THE GALVANIC CURRENT.

Among the various derivatives of the series  $\text{C}_n \text{H}_n \text{O}_4$ , few have created more interest than the substances which Dr. Kolbe‡

\* Again referring to Mr. Morley's paper on propione derived from propionic acid, we find he gives  $100^{\circ}\text{C}$ . as the boiling point of propione, which is the correct number assigned by theory. It is natural to suppose that, as propione is the intermediate term between the ketones of acetic and butyric acids, its boiling point should also be equidistant from those of its neighbours in the system; this is actually the case, as seen from the comparison appended—

Acetone	-	-	$\text{C}_3 \text{H}_3 \text{O}$ , $56^{\circ}\text{C}$ .	} diff. 44
Propione	-	-	$\text{C}_5 \text{H}_5 \text{O}$ , $100^{\circ}\text{C}$ .	
Butyrone	-	-	$\text{C}_7 \text{H}_7 \text{O}$ , $144^{\circ}\text{C}$ .	

We may fairly presume that Frémy's propione is either a mixture containing propione as one of its constituents, or a definite compound closely allied to, but differing in composition from, the true propione.

† Benzoic acid	-	$\text{C}_{14} \text{H}_6 \text{O}_4$	Valeric acid	-	-	$\text{C}_{10} \text{H}_{10} \text{O}_4$
Nitrobenzoic acid	$\text{C}_{14} \left\{ \begin{smallmatrix} \text{H}_5 \\ \text{NO}_4 \end{smallmatrix} \right\} \text{O}_4$		Nitrovaleric acid	-	$\text{C}_{10} \left\{ \begin{smallmatrix} \text{H}_9 \\ \text{NO}_4 \end{smallmatrix} \right\} \text{O}_4$	
Carbanilic acid	$\text{C}_{14} \left\{ \begin{smallmatrix} \text{H}_5 \\ \text{NH}_2 \end{smallmatrix} \right\} \text{O}_4$		Carbobutylic acid	-	$\text{C}_{10} \left\{ \begin{smallmatrix} \text{H}_9 \\ \text{NH}_2 \end{smallmatrix} \right\} \text{O}_4$	
Aniline	-	$\text{C}_{12} \text{H}_7 \text{N}$	Butylamine (Petanine)	$\text{C}_8 \text{H}_{11} \text{N}$		

‡ Chem. Soc. Mem. III. 378.



has obtained in the electrolysis of acetic, butyric, and valeric acids. In subjecting the potassa-salts of these acids to the current, he formed, among other products, the compounds :

Methyl	-	-	$C_2 H_3$
Propyl	-	-	$C_6 H_7$
Butyl (Valyl)	-	-	$C_8 H_9$

which he considers as the radicals of methylic, propylic, and butylic (valylic) alcohols. Several analogous substances, such as ethyl and amyl, having lately been obtained by Dr. Frankland\* in a totally different mode of decomposition from actual alcohol-compounds, it appeared of some interest to extend the galvanic process to a case which would yield a product previously formed by the chemical method. For this purpose, we have studied the action of the pile upon caproic acid, whose decomposition promised to furnish the compound amyl,  $C_{10} H_{11}$ , previously obtained by Dr. Frankland† from iodide of amyl.

The apparatus used in the decomposition of caproate of potassa, prepared from pure caproic acid boiling at  $198^\circ$ , was perfectly similar to that minutely described in Dr. Kolbe's memoir. When six of Bunsen's zinco-carbon elements were employed, the decomposition of the concentrated solution of caproate of potassa succeeded without difficulty. The liquid rapidly assumed a milky appearance from the separation of numerous gas bubbles and small oily droplets, which gradually collected as a layer of oil upon the surface of the liquid contained in the decomposition-apparatus.

The gases disengaged consisted chiefly of carbonic acid and hydrogen, mixed, however, with a compound imparting to them a peculiar aromatic odour.

The oily liquid, when separated by means of a pipette and subjected to distillation, began to boil between  $125^\circ C.$  ( $257^\circ F.$ ) and  $160^\circ C.$  ( $320^\circ F.$ ). It was evident that, as was the case in the corresponding decomposition of valeric acid, this liquid consisted of a variety of products. Only a limited quantity being at our disposal, we at once resorted to the process of purification pointed out by Dr. Kolbe. For this purpose the liquid was distilled with an alcoholic solution of potassa, when a potassa-salt remained in the retort, which, on addition of a mineral acid, yielded an oily acid. Although we have not made an analysis of this substance, we have no doubt that it was caproic acid; we may here adduce the analogous formation of the acids, both in the valeric, as stated by Dr. Kolbe, and in the cenanthylic series, as proved by our own experiments, detailed hereafter.

The alcoholic distillate yielded with water a light aromatic liquid, which was separated by a tap-funnel, and dried over chloride of

\* Chem. Soc. Qu. J. III. 362.

† Chem. Soc. Qu. J. III. 30.



calcium. When subjected to ebullition, it commenced boiling at 150° C. (302° F.), the boiling-point becoming stationary at 155° C. (311° F.), when a fraction was collected separately. At 160° C. (320° F.), every drop had passed over.

The liquid distilling at 155° possessed all the properties assigned by Frankland to the compound obtained in the decomposition of iodide of amyl by metallic zinc.

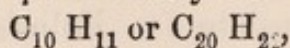
When subjected to combustion with protoxide of copper, the following numbers were obtained :

I. 0.1996 grms. of substance gave :		
0.6171	„	carbonic acid.*
II. 0.2130 „ substance gave :		
0.6579	„	carbonic acid, and
0.3010	„	water.

Percentage-composition :

		I.	II.
Carbon	- -	84.32	84.23
Hydrogen	- -	—	15.70

These numbers correspond closely with the formulæ :



as may be seen from the following comparison :

		Theory.	Mean of Experiment.
10 eqs. of Carbon	-	60    84.50	84.26
11 „ Hydrogen	-	11    15.50	15.70
1 eq. of Amyl	-	71    100.00	99.96

These results leave no doubt that the substances obtained in the electrolysis of caproic acid and in the decomposition of iodide of amyl are identical ; and hence we may assume generally that the action of zinc upon an alcohol-iodide ( $C_n H_{(n+1)} I$ ), and the electrolysis of an acid  $C_{(n+2)} H_{(n+2)} O_4$ , give rise to the formation of the same compound.

The products collected above and below amyl, contain other products besides amyl ; but we are not at present in possession of sufficient data to form a correct idea respecting the nature of these substances. From the analogous observations of Dr. Kolbe in the valeric series, we should expect to meet in the lower fraction, the hydrocarbon  $C_{10}H_{10}$  and fusel-oil, arising from the decomposition of the compound ether,  $C_{10}H_{11}.C_{12}H_{11}O_4$ , by the contact of the crude oil with potassa. We have not as yet studied this question with sufficient accuracy ; but it may be even now stated that, in the lower fraction, we have not, up to the present moment, been able to detect fusel-oil. Moreover, the existence of an ether  $C_{10}H_{11}.C_{12}H_{11}O_4$ , in the crude product of electrolysis, is not supported by the results of observation : for this

\* Hydrogen lost.



compound ether, which would be nothing else than the caproate of amyl, prepared by us as stated above, boils at  $211^{\circ}$  C. ( $411^{\circ}8$  F.), whilst the crude product entirely distilled below  $180^{\circ}$  C. ( $356^{\circ}$  F.). However, we leave this question open, and are satisfied to have established by experiment, the analogy of the principal metamorphosis of valeric and caproic acids, under the influence of the galvanic current.

DECOMPOSITION OF CENANTHYLIC ACID UNDER THE INFLUENCE  
OF THE GALVANIC CURRENT.

Incidentally to the experiment with caproic acid, we have also subjected cenanthylic acid to the action of the pile.

The acid which served us for the experiments communicated in the remaining portion of our paper was prepared in the manner recommended by Tilley,\* by acting upon the oil of *Ricinus communis* with dilute nitric acid. By this means, with considerable patience, a sufficient amount was obtained. We have tried various other processes, oxidation of the oil with chromic acid, or a mixture of bichromate of potassa with sulphuric acid, or treatment of cenanthale with various oxidizing agents; but we have invariably found that the action of nitric acid on the oil, although tedious in the extreme, still gives the best results. The crude acid was repeatedly washed, and afterwards redistilled with water, in order to insure its perfect purity. As it is partially decomposed by distillation alone, we tested its purity by the analysis of a silver-salt in preference to taking the boiling-point.

0.2324 grms. of silver-salt gave :  
0.1052 „ silver,  
yielding a percentage of 45.30 of silver.  
Theory requires 45.56 of silver.

The potassa-salt was easily made by neutralizing the acid with pure carbonate of potassa. This salt is not crystallizable; it is easily soluble in water.

The phenomena, observed in the decomposition of cenanthylic acid, are perfectly analogous to those exhibited in the electrolysis of caproic and valeric acid—evolution of carbonic acid and hydrogen, separation of an oily layer in the decomposing apparatus, and formation of carbonate and bicarbonate of potassa in the residuary aqueous solution.

The oily layer, which had an ethereal odour and a sweetish taste, was separated, dried, and subjected to distillation. It boiled between  $130^{\circ}$  ( $266^{\circ}$  F.) and  $230^{\circ}$  ( $446^{\circ}$  F.), the thermometer exhibiting a tendency to become stationary towards  $190^{\circ}$  ( $374^{\circ}$  F.). Near the close of

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\* Chem. Soc. Mem. I.



the operation, the liquid assumed a dark-brown colour, and a considerable quantity of charcoal remained in the retort. The separation of the various constituents of the oil was effected by treatment with an alcoholic solution of potassa, exactly as in the product obtained from caproic acid.

However, as we performed these experiments upon a somewhat larger scale, we took care to establish by analysis the nature of the acid remaining in form of a potassa-salt. For this purpose, the acid was separated by hydrochloric acid, washed, converted into the ammonia-salt, and subsequently into the silver-salt.

0.4965 grms. of silver-salt gave :  
 0.2260 „ silver = 45.51 per cent.  
 Theory requires 45.56 per cent.

These numbers establish beyond doubt, the separation of ænanthylic acid by potassa, from the crude-oil product.

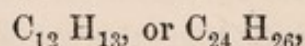
The alcoholic distillate, when treated with water, yielded an oily liquid, which, after being dried with chloride of calcium, boiled between 170° (338° F.) and 210° (410° F.); by far the largest quantity, however, distilled at 202° (395.6° F.). In fact, the thermometer became stationary at this temperature, even in the first rectification. The fraction collected round this point, when distilled, once more exhibited a perfectly constant boiling-point at 202° (395.6° F.). This liquid had a very agreeable aromatic odour: it was insoluble in water, but miscible in all proportions with alcohol and ether. Analysis gave the following results:

I. 0.2245 grms of substance gave :  
 0.6940 „ carbonic acid, and  
 0.3160 „ water.  
 II. 0.3345 „ substance gave :  
 1.0370 „ carbonic acid, and  
 0.4650 „ water.

Percentage-composition :

		I.	II.
Carbon	- -	84.49	84.54
Hydrogen	- -	15.60	15.44

These numbers correspond closely with the formulæ,



as may be seen from the following comparison :

		Theory.	Mean of experiment.
12 eqs. of Carbon	-	72	84.70
13 „ Hydrogen	-	13	15.30
1 „ Caproyl	-	85	100.00



The formula  $C_{12}H_{13}$ , homologous to those of methyl, ethyl, &c. would represent the radical of an alcohol,  $C_{12}H_{14}O_2$ , standing to caproic acid in the same relation as acetic acid stands to wine-alcohol. This alcohol might be termed caproylic alcohol, and the corresponding radical hydrocarbon, caproyl. The nomenclature of this series is so sadly embarrassed by the accumulation of similar names in the eighth and tenth family, that—objectionable though the rechristening of chemical compounds may be—we believe that the suggestion of more appropriate names for caprylic and capric acids, would meet the general approbation of chemists.

It would have given us much pleasure to have studied the deportment of caproyl under the influence of re-agents, the more so, as the opinions of chemists are divided respecting the formulæ of the so-called radicals, some of them adopting expressions corresponding to 2 volumes of vapour, others preferring 4 volumes in a formulæ. The study of the products of decomposition of caproyl might have decided this question; but unfortunately the limited quantity of substance at our disposal prevented us from following out this direction of the inquiry. Moreover, caproyl exhibits but little disposition to furnish readily accessible products.\*

We mention only that the substance is not affected by concentrated sulphuric acid, and that it may be distilled with moderately concentrated nitric acid, without undergoing any change. It was only by distillation with a mixture of the two acids, that a very slow, and even then incomplete oxidation took place. After repeated distillation, the distillate was mixed with water; the supernatant oil, separated by a pipette, and heated with ammonia, dissolved but partially. The ammoniacal solution contained an oily acid, which separated on addition of a mineral acid, and exhibited the odour of caproic acid. We converted the remaining solution, after boiling off the excess of ammonia, into a silver salt, which was deposited as a

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\* The remarkable unalterability of the so-called radicals, when contrasted with the want of stability of the higher homologues of marsh-gas—as indicated by the non-production of these substances in the reaction of alkaline earths upon the higher terms of the series  $C_nH_nO_4$ —appear to discountenance more and more the assumptions of the identity of the two classes of compounds. As I had an opportunity of suggesting at an earlier period (*Chem. Soc. Qu. J.* III. 133), the radicals may be only isomeric with the marsh-gas series. This, of course, does not interfere in the slightest degree with the adoption of 4 volume formulæ; nor does the conversion of caproyl into caproic acid, which I consider established by the experiments of Messrs. Brazier and Gossleth, in my opinion, militate in the slightest degree against the admission of the higher formulæ.—*Note by Dr. Hofmann.*



whitish, very difficultly soluble powder. After recrystallization, it was obtained in slightly yellow crystals, which gave on analysis the following results:

I. 0.2145 grm. of silver-salt gave:  
0.1055 „ silver.

A second specimen prepared in a similar manner, was analysed in the same way; during ignition a slight deflagration took place.

II. 0.1486 grm. of silver-salt gave:  
0.0686 „ silver.

Percentage:

	I.	II.
Silver - - -	49.13	46.16

The theoretical percentage of silver in the caproate is 48.65, and in the nitrocaproate 40.30; the first analysis exhibits a slight excess, which may be due to reduction of a small quantity of silver during the recrystallization of this rather difficultly soluble salt. The deficiency of the second may possibly be owing to the presence of a small quantity of nitrocaproic acid, a supposition which is supported by the slight deflagration during combustion, and by an analogous observation of Dr. Kolbe,\* in the oxidation of butyl. We are sorry that our results are not more definite, but hope their insufficiency will be excused by the difficulty attending these operations. We have no doubt in our own minds that the acid produced under these circumstances is caproic acid.

Bromine has scarcely any action upon caproyl, not even under solar irradiation.

Chlorine acts very powerfully even in diffused day-light, torrents of hydrochloric acid being immediately disengaged. The caproyl is rapidly converted into a viscous mass, which, being decomposed on ebullition, with evolution of hydrochloric acid and deposition of carbon, could not be purified for analysis. Even by a very moderate action of chlorine, we did not succeed in obtaining a direct compound of caproyl with chlorine.

In conclusion, we have to add that we have made a few experiments with the oil which passed over before caproyl, in the rectification of the liquid separated from the alcoholic distillate after treatment with potassa. This substance, which has an aromatic odour and sweet taste, was several times redistilled, when a compound was

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\* Chem. Soc. Qu. J. II. 163.



obtained boiling pretty constantly at  $175^{\circ}$  ( $347^{\circ}$  F.). Analysis with protoxide of copper gave the following results :

0.3220 grm. of substance gave :  
 1.0070 „ carbonic acid, and  
 0.4225 „ water.

Percentage-composition.			Theoretical values of $C_n H_n$ .		
Carbon	-	85.29	Carbon	-	85.72
Hydrogen	-	14.57	Hydrogen	.	14.28

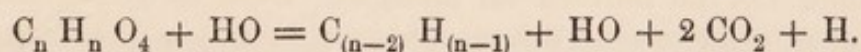
These numbers show that the liquid in question is a hydrocarbon of the family  $C_n H_n$ , the slight deficiency in the carbon and the excess in the hydrogen, being evidently due to the presence of a trifling quantity of caproyl.

We have no direct data for the value of  $n$ ; the boiling-temperature would point to the formula  $C_{24} H_{24}$ .

We have not met among the products obtained in the electrolysis of cenanthylic acid, with the hydrocarbon caproylene (oleylene),  $C_{12} H_{12}$ , or with caproylic alcohol, the formation of which substance we might have expected from the analogous deportment of valeric acid; we cannot, however, adduce any positive evidence as to the absence of small quantities of these substances. The question, what compound in the crude oil gives rise to the formation of the cenanthylic acid, whether it be a kind of compound ether or an aldehyde, &c. has still to be answered by further experiments.

One point, however, appears to be fixed by the preceding experiments, namely, that the members of the series  $C_n H_n O_4$ , when treated with the galvanic current, invariably give rise to the formation of a hydrocarbon closely connected with the series following one step lower on the scale of organic compounds, hydrogen and carbonic acid being simultaneously eliminated.

Generally expressed, this metamorphosis would be represented by the following equation :



This equation shows that formic acid, when exposed to the current, can yield only hydrogen and carbonic acid. Together with this principal metamorphosis, several secondary changes appear also to occur, whose nature, however, is not yet perfectly understood. It deserves, moreover, to be noticed, that these latter changes, far from presenting the constant character of the chief decomposition, appear to vary with the position of the substances examined upon the ladder of combustion.



the function  $f(z)$  is analytic in the region  $R$  and  $f(z)$  is not constant, then  $f(z)$  is one-to-one in  $R$ .

Let  $f(z)$  be a function analytic in the region  $R$  and let  $f(z)$  be not constant. Then  $f(z)$  is one-to-one in  $R$ .

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