CXCVII. *Upon the Chemical Constitution of Metacetic Acid, and some other Bodies related to it.* By E. FRANKLAND, Esq. and H. KOLBE, Ph.D.

THE researches into the constitution of organic compounds certainly belong to the most interesting in chemistry. But they are always attended with more or less danger, and those who, leaving the safer road of experiment, plunge into the depths of hypothesis, and build up theories apparently ingenious, though often untenable, frequently stumble and fall amongst a host of contradictions. It is a common error,

as experience teaches, into which young chemists are very apt to fall, that, persuaded of the infallibility of their own views, and blind to well-founded objections, they endeavour to convince by quick and ready argument rather than by solid reasoning, and consequently they either offend others or feel themselves offended when contradicted.

When in the face of this danger we endeavour to advance views concerning the rational composition of some organic acids which do not accord with those generally received, we do it with a certain degree of timidity, and with the most strenuous endeavour to avoid those causes of error which have been pointed out. It is far from our intention to give a decided preference to the mode of viewing the subject here proposed, or indeed in any way to force our own opinion, nor is it unknown to us that even these views leave many facts unexplained; but we feel convinced that no detriment can accrue to the progress of science by looking at subjects of such importance with an impartial eye from all possible sides.

The starting-point of our experiments was the idea recently expressed by Berzelius, that acetic acid might be considered as a conjugate oxalic acid, as methyl oxalic acid, $C_2 H_3 C_2 O_3$. If this view of the subject, which explains so readily the conversion of acetic acid into chloracetic acid, and the remarkable reconversion of the latter into the former, and which has been further confirmed by the analogous relations of chlorocarbohyposulphuric acid and methyl-hyposulphuric acid, is correct, then the question arises whether it might not be extended to those other acids, so nearly related to acetic acid, namely, formic acid, metacetic acid, butyric acid, benzoic acid, &c. We are of opinion that this question cannot *à priori* be answered in the negative; on the contrary, it appeared to us, after pursuing the subject further from that point of view, that the manifold metamorphoses which the above combinations undergo might be explained in a very simple manner, and we consequently have submitted the question to careful experimental examination; and we believe that we have gained a fact in support of the theory of conjugate compounds in its application to the acids in question, by the action which cyanide of ethyl exhibits with alkalies and acids.

When benzoic acid is supposed to consist of oxalic acid with the carburetted hydrogen, $C_{12} H_5$ (phenyle), as a conjunct, then it is evident that benzoic-nitrile obtained by Fehling* in distilling benzoate of ammonia, must be a cyanogen compound of the same carbo-hydrogen $= C_{12} H_5 Cy$. This mode of decomposition of phenyle-oxalic acid becomes thus

* Liebig's *Annalen*, xlix. p. 91.

completely analogous to the well-known formation of cyanogen by heating oxalate of ammonia, and to the formation of hydrocyanic acid from the formiate of ammonia.

Benzoe-nitrile, viewed as cyanide of phenyle, would then, together with the analogous body recently discovered by Schlieper*, valero-nitrile (C_8H_9Cy , cyanide of valyle), become allied to cyanide of ethyl; and as these bodies in contact with alkalies are so easily transformed into benzoic acid and valerianic acid, it is to be presumed that cyanide of ethyl under similar circumstances would become transformed into ammonia and metacetic acid.

We prepared for this purpose pure cyanide of ethyl, according to the process of Pelouze, by the distillation of sulphovinate of potash with cyanide of potassium. The yellow-coloured liquid which passes over† was mixed with water, and separated again by chloride of sodium, dried over chloride of calcium, and lastly distilled in a bent tube freed from air and hermetically sealed. Purified in this manner cyanide of ethyl is a limpid colourless liquid, having an odour much resembling that of the terrible cacodyl. The analysis of the substance gave the following numbers:—

0.219 grm. gave 0.523 grm. of carbonic acid and 0.186 grm. of water.

Carbon . .	65.19	6	Theory. 65.45
Hydrogen . .	9.46	5	9.09
Nitrogen . .	25.35	1	25.46

To settle the question started above, this cyanide of ethyl was added drop by drop to a tolerably concentrated boiling solution of caustic potash, and the product of distillation returned to the retort as long as it retained any smell. During this operation a considerable portion of ammonia was given off. The alkaline residue distilled with sulphuric acid produced an acid liquid, which, neutralized with carbonate of silver, baryta, or lead, gave the corresponding salts of those bases. We had previously satisfied ourselves, by a carefully conducted experiment, that no formic acid was present in the acid solution.

The silver salt crystallizes from its aqueous solution in small acicular prisms. It is sparingly soluble in water, and the solution becomes blackened on boiling. The crystals dried over sulphuric acid *in vacuo* had the composition of metacetonate of silver.

* *Annalen der Chemie*, lix, p. 15.

† We found, in contradiction to Pelouze's statement, that cyanide of ethyl is tolerably soluble in water; but when the solution is saturated with common salt, it again separates unchanged and comes to the surface.

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I. 0.211 grm. gave, when burnt with oxide of copper, 0.153 grm. carbonic acid and 0.055 grm. water.

II. 0.167 grm. gave on careful ignition 0.100 grm. of metallic silver.

Carbon . . .	19.77	6	19.90
Hydrogen . .	2.89	5	2.76
Oxygen . . .	13.06	3	13.27
Oxide of silver .	64.28	1	64.07
	<u>100.00</u>	<u>15</u>	<u>100.00</u>

The salt of barytes is very soluble in water; the solution of the salt evaporated to dryness and dried for a long time at 212°, gave the following numbers:—

I. 0.339 grm. gave 0.311 grm. carbonic acid and 0.116 grm. water.

II. 0.258 grm. gave 0.211 grm. sulphate of baryta.

			Theory.
Carbon . . .	24.98	6	25.46
Hydrogen . .	3.79	5	3.53
Oxygen . . .	17.58	3	16.99
Barytes . . .	53.65	1	54.02
	<u>100.00</u>		<u>100.00</u>

The lead compound has the sweet taste of acetate of lead: it does not appear to crystallize, but dries up to a tough amorphous saline mass. A portion dried at 212° and *in vacuo* gave exactly the quantity of oxide of lead, corresponding to the formula $\text{PbO}, \text{C}_6 \text{H}_5 \text{O}_3$, namely,—

0.446 grm. gave 0.282 grm. oxide of lead and 0.021 grm. metallic lead, equivalent to 63.40 per cent. instead of 63.19.

From the above analyses, there can be no doubt that the acid product of the action of caustic potash upon cyanide of ethyl is metacetic acid. The same result is produced by weak sulphuric acid (1 part acid to 2 parts water). The silver salt prepared from the acid product of distillation in this case exhibited the properties described above, and an estimation of the oxide of silver gave the following result:—

I. 0.150 grm. when ignited gave 0.090 grm. metallic silver, corresponding to 64.30 per cent. oxide of silver; the theoretical proportion being 64.07 per cent.

The mode of decomposition of cyanide of ethyl described is therefore quite analogous to that of benzoe-nitrile and valero-nitrile; and if metacetic acid is considered as ethyl oxalic acid, with the formula $\text{C}_4 \text{H}_5 \text{C}_2 \text{O}_3$, the decomposition may be expressed by the equation

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The assumption will be rendered still more palpable, if, as there is little doubt, at a future period we are able again to produce cyanide of ethyl from metacetate of ammonia.

If, on the contrary, metacetic acid is considered as an oxide of the radical C_6H_5 , then it must be assumed, that during the process of oxidation the two atoms of carbon, in the cyanogen, amalgamate themselves, as it were, with ethyl, in order to form the new radical metacetyl. Setting aside the great improbability attached to such an assumption, to which there would be at present no analogous case, we feel justified in giving preference to the former explanation, because it is the more simple, and because it completely agrees with the known transformation of cyanogen and water into oxalic acid and ammonia; and if, as one of us has found, valerianic acid, placed in the circuit of the voltaic current, by the assumption of 1 atom of oxygen, becomes converted into carbonic acid and the carbo-hydrogen C_8H_8 , we consider that our view has gained by that fact an additional support, and that the acid in question contains that carbo-hydrogen in conjugate combination with oxalic acid.

The foregoing observations lead to a great simplification of our hypothesis in regard to organic radicals, inasmuch as they do away with the necessity of supposing a specific radical for each acid belonging to an alcohol. The series of radicals which are produced by the addition of one or more equivalents of the carbo-hydrogen C_2H_2 to 1 equivalent of hydrogen, namely C_2H_3 , C_4H_5 , &c., the hydrated oxides of which form the alcohols, are again found in accordance with our view in the acids derived from them, conjoined with oxalic acid. It may be conceived that the oxygen, in converting alcohol or oxide of ethyl into acetic acid, first acts upon the equivalent of carbo-hydrogen C_2H_2 , which alone distinguishes ethyl from methyl, and that the successive products of oxidation of this body take up the remaining radical methyl into conjugate combination; thus in the formation of aldehyde and acetic acid,

Moreover, it cannot be denied that our ideas concerning the functions performed by compound radicals are very much enlarged by these considerations. For when we find methyl and ethyl combining like the electro-positive inorganic elements with the electro-negative non-metallic substances, the

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property which they also exhibit of uniting with oxalic acid, hyposulphuric acid, and with other, perhaps even neutral, bodies to form conjugate compounds, evinces such an extensive range of properties as is nowhere to be met with amongst the more narrowly defined powers of combination of inorganic substances ; and it is probable that nature, when she brings forth the innumerable and manifold products of the organic kingdom by a wonderful combination of those few elements which are at her disposal, may likewise make use of these supposed extensive combining powers of the organic radicals, as the simplest means of accomplishing her greatest works.

We beg to express our warmest thanks to Dr. Lyon Playfair for the use of his laboratory and apparatus in carrying out the above investigation, and for the uniform kindness which we as his assistants have experienced at his hands.