

On Dry Distilled Racemic Acid

J. J. BERZELIUS*

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INTRODUCTION

The products resulting from the dry distillation of organic substances have recently been the object of particularly thorough study. Mention may be made of Faraday's investigation of the several forms of carbon-bound nitrogen obtained in this way, Bussy and Lecanu's of the distillation products of fatty oils, Riechenbach's of the products obtained from beech-wood and Pelouze's of the distillates of tannins, pyrogallic acid and malic acid. Despite the fairly important findings that have then been made, it is evident that this subject is still in its cradle, and that the so-called dry distillation of organic substances opens up an entirely new field in chemistry.

It is namely not only by means of the distillation of various substances, or of a mixture of several organic substances, that different products are formed, but the same substances — or mixtures of substances — may give rise to different products, according to temperature and the admixture of different inorganic substances.

It is easily realized that if one would undertake to study the dry distillation of a certain substance — for example, cane sugar — under all these varying conditions, a number of different compounds would be formed, among them perhaps many as yet unknown. If one then undertook the similar treatment of one unmixed substance after the other, it is impossible to predict the number of substances that would be produced in this way. It is nevertheless evident that if one would first study the special distillation of each organic substance, it would then be all the easier to analyze the products of their mixtures, *e.g.* woods, seeds, leaves, *etc.*, that are distilled.

* The Editor presents here a translation of the handwritten original of Berzelius' communication to the Swedish Academy of Science in 1835 concerning his discovery of pyruvic acid and its preparation and properties. The paramount interest taken in this compound by the biochemists of today may justify a reproduction of Berzelius' paper. It may also be of interest to note that he, when he in 1835 created the concept of catalysis, metal catalysis in chemistry and enzyme catalysis in biology, claimed that "the catalytic force . . . functions largely in the same manner as heat". Here his experimental skill allowed him to produce at 200°C and to isolate the same labile compound, which much later was shown to be produced by enzymes when sugar and similar substances are burnt at ordinary temperature in the living organisms.

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The excellent investigations for which we are indebted to Pelouze, of the dry distillation of pyrogallic acid and malic acid, prompted me to resume an interrupted study of the distillation products of tartaric acid and racemic acid, in particular of the latter. Since, in the course of this work, I found myself forestalled by the same distinguished chemist, I can only hope that the ears I have plucked on the field left by him are not entirely without value.

ON PYRUVIC ACID AND THE CHANGES WHICH OCCUR WHEN RACEMIC ACID IS SUBMITTED TO DRY DISTILLATION AT A TEMPERATURE NOT EXCEEDING $+ 250^{\circ}\text{C}$.

In the report of my investigation of the composition of tartaric acid and racemic acid, which I had the honour to present to the Royal Swedish Academy of Sciences in 1832, I pointed out that racemic acid on dry distillation produces an acid different from the pyrotartaric acid arising from tartaric acid, which has been well known for a long time.

This pyrotartaric acid was intensively studied first by Gruner and then by Pelouze, who showed that the distillation products of tartaric and racemic acids are the same, mainly pyrotartaric acid and acetic acid, the latter in such a high concentration that it almost crystallizes out. Although I have confirmed the findings of Pelouze that tartaric acid and racemic acid give the same distillation products, I did not reach the same conclusion that he did concerning the nature of the main part of the distillate, which he considered, because of its smell, to consist of acetic acid. This acid is the same as that which I originally thought to be formed from racemic acid alone, which I called pyruvic acid and described as a volatile acid.

I will go on using the name pyruvic acid, *acidum pyruvicum*, as an indication of its origin from the grape. The same acid is also found in the acidic fluid which is formed when solid potassium tartrate is submitted to dry distillation; it consequently occurs in an ancient remedy, *mixtura diatrion* or *m. pyrotartarica* and deserves to be known for this reason as well.

I distilled a sample of tartaric acid in a tubulated glass retort on a sand bath, the temperature of which could be kept almost constant by increasing or reducing the draught. The mass started to give off a water clear distillate of a sharp taste, smelling of acetic acid, whereupon it melted, turned grayish, and began to foam.

When the material showed a tendency to boil over, the cork was removed from the tubular extension and a rigid platinum wire was introduced to break the foaming, which was easily accomplished. It was sometimes necessary to repeat this procedure. Without this precaution the distillation proceeds extremely slowly and the entire foaming mass collects in the upper part of the retort leaving the lower part empty. During the operation carbon dioxide is developed in a continuous stream, necessitating tubulation of the receiver, the end of the tube being submerged in water.

The content of the retort gets very sticky before the end of the operation, mostly due to condensed pyruvic acid. Later on in the operation the distillate gets more and more concentrated, and becomes yellow in colour, but even at the end is no more than pale yellow if the temperature does not exceed $+ 220^{\circ}$

(Celsius). The residue in the retort becomes more and more sticky, finally changing to a fluid which boils without foaming; the temperature is then about $+200^{\circ}$, and when the boiling is finished and nothing more distils at $+200^{\circ}$ the operation is finished. There is then left in the retort a mass which is soft while still hot but after cooling behaves like carbon.

The distilled acid contains no oil although the last fraction becomes slightly cloudy on dilution with water. It has an acetic acid like smell although slightly burned, a burning sharp acid taste, a consistency like sulfuric acid, and a yellow colour. If it is distilled over a water bath, which proceeds very slowly, one gets at first a colourless acid smelling strongly of acetic acid but also slightly of formic acid. The distillate usually turns yellow and assumes a thick consistency. In the last viscous fraction I found a specific gravity of 1.2792 or even slightly more. During the procedure carbon dioxide gas develops continuously, although no gas bubbles can be seen in the liquor, and the carbon dioxide must be given a possibility to escape; the fluid in the retort darkens more and more, finally turns dark brown and leaves a residue of a resinous mass at the end of the distillation. *Sometimes in my experiments the syrupy distillate, on cooling, was completely filled with crystals of pyruvic acid*, but this happened only half the number of times that I repeated the process. Before the distillation this pyrotartaric acid (?) was dissolved in the fluid together with part of the brown sticky material, most of which is formed during the redistillation; new quantities of this material are formed each time the distillation is repeated.

I have tried to redistil the acid in an apparatus from which I had removed the air in order to find out whether the air exerted any influence on its formation; the result, however, was the same, the only difference was that the distillation proceeded much more slowly. When the apparatus was opened carbon dioxide gas escaped with an explosion and showed that an increased pressure of carbon dioxide gas was the reason for slowing up the distillation. A considerable quantity of the resinous mass remains after distillation indicating that the acid after a few redistillations would soon be destroyed. The test with silver carbonate (carbonated silver oxide) indicated that formic acid could be present in the distillate. However, the salts prepared with sodium hydroxide and lead oxide always indicated the presence of acetic acid through their solubility in alcohol in which the lead salt of formic acid is almost insoluble. Also the acid does not become opalescent on boiling.

Since an attempt to obtain *the free acid* from its sodium salt, through distillation with sulfuric acid, failed, while the acid was almost completely destroyed, I had to find another way to obtain pure acid in a fairly strong concentration. This can be achieved in the following way. Freshly precipitated lead carbonate is dissolved in the redistilled acid to full saturation; at first the oxide dissolves but later on it is precipitated as a granular powder increasing in amount during 48 hrs, particularly in the cold. It is collected on a filter paper and washed.

The lead salt is suspended in a minute quantity of water, treated with hydrogen sulphide and strained through cloth. The lead sulphide is pressed and the mother liquor evaporated over sulfuric acid *in vacuo*. A thick syrup results which finally (unreadable). No gas is evolved during this

concentration. A certain amount of the acid disappears, however, because of its volatility.

The properties of the acid are as follows: thick syrup which can be drawn out in threads, weak but sticky acid smell, strongly acid, later bitter taste. Turns fluid in the air. Soluble in alcohol and ether. On heating it partly evaporates and partly disintegrates, as previously described. The composition and the degree of saturation of this acid were elucidated through the analyses of its silver and sodium salts. The analyses were as follows: 0.31546 g acid produced with copper oxide 0.5225 g carbonic acid and 0.0145 g water. It gave in per cent:

	Found	Atoms	Calculated
Carbon	45.80	6—458.628	46.042
Hydrogen	3.68	6— 37.488	3.463
Oxygen	50.52	5—500.000	50.195
	<u>100.00</u>	<u>999.116</u>	<u>100.00</u>

Its formula is consequently $C_6H_6O_5$. Upon comparison of this formula with that of tartaric acid and racemic acid, which is $C_4H_4O_5$, one finds that *this acid can be considered to be a lower degree of oxidation of the same radical*. On the same quantity of oxygen it contains one and a half times as much of the radical as do the tartaric and racemic acids, giving a formula for the latter acids $2 CH + 5 O$, while the formula for the pyruvic acid is $3 CH + 5 O$.

One could say that formic acid, tartaric acid, pyrogallic acid and pyruvic acid are derived from the same radical giving them the following composition:

Pyrogallic	acid	3 CH + 3 O
Pyruvic	»	3 CH + 5 O
Racemic and tartaric	»	2 CH + 5 O
Citric	»	2 CH + 4 O
Formic	»	CH + 3 O

Berzelius goes on to describe in six large pages no less than 20 different metal salts of the new acid, all prepared and analyzed by himself. It is very typical of this tremendously diligent and ambitious chemist that he did not feel satisfied until he had prepared the potassium, sodium, silver, ammonium, barium, strontium, calcium, aluminium, beryllium, ytterbium, thorium, manganese, iron, cobalt, mercury, lead, basic lead, uranium, copper, platinum, and gold salts of his new acid.

As is evident, Berzelius interpreted the structure of the pyruvic acid in accordance with the ruling concepts of those days. He considered the acid to be an oxide of an organic radical, the ethine radical C_2H_2 , here written as CH, assumed to be common to a series of well known organic acids. In spite of the improvement Berzelius made of the quantitative organic analysis by introducing the use of the calcium chloride tube for the collection of the water of combustion, his technique of analysis was by far not so accurate in the organic field as it was in the inorganic. Hence the misleading figures, which allowed him to draw the wrong conclusions. On another occasion the theory about organic radicals influenced Berzelius' thinking, namely when in 1838 he suggested the name "protein" for a new radical, that the Dutch chemist Mulder claimed that he had found in all kinds of animal and plant material.