

BOOK V

INTRODUCTION

965. Chemists who follow Stahl's¹ approach and believe that the acid obtained when distilling oil is one of the constituent principles of that oil, have in general regarded this acid as the cause of the reaction of oils with alkalis. Later, Berthollet² felt that this reaction depended on the affinity of the oils themselves for alkalis. He rightly regarded soaps as compounds in which bases capable of forming salts have been neutralized by fatty materials acting like acids. CErsted³ has expressed the same opinion. Finally, some chemists suggested that oil could not be saponified without absorbing oxygen but failed to support this idea with any factual evidence⁴. This was the state of the art when I started working on oils and fats. In this book, I will devote myself to explaining the change in composition that many fatty materials undergo when treated with alkali, a change that constitutes *saponification*. I will consider this treatment from two general points of view: 1. *with respect to the fatty materials*; 2. *with respect to the alkalis*.

PART ONE

SAPONIFICATION CONSIDERED WITH RESPECT TO THE FATTY MATERIALS

966. Before making use of the facts that have been disclosed in the previous books⁵ and that must serve as the basis of a theory of saponification, we must investigate: 1. whether any acetic acid is produced during this process; 2. whether carbon dioxide is formed; 3. whether contact with oxygen is necessary for it to occur.

CHAPTER 1⁶

§ 1. IS ANY ACETIC ACID PRODUCED DURING SAPONIFICATION ?

967. Knowing that potassium hydroxide obtained as alcoholic extract⁷ often contains acetic acid, I saponified of 190 g of lard with potassium hydroxide made by causticization with lime⁸: the resulting soap was acidulated with tartaric acid and the resulting aqueous liquid distilled. After the distillation product had been neutralized by baryta water, it yielded only 10 mg of dry acetate which is such a small amount that it can be disregarded, whatever its origin*. When I saponified the same amount of fat with pure caustic potash, the soap yielded 150 mg barium acetate. In comparison with 190 gram of fat, this amount is still quite small and in comparison with the centigram⁹ obtained from the soap formed by the causticized potash, shows that 'alcoholic' potassium hydroxide can introduce some acetic acid into the saponification products.

§ 2. IS ANY CARBON DIOXIDE PRODUCED DURING SAPONIFICATION ?

968. To resolve this question, I used a bell jar with a diameter of 3 cm and a height of 30 cm. I filled it with warm (28°C) mercury until there remained just enough room for exactly 16.5 g of molten fat. After this had been introduced into the jar, I closed it with a glass stopper and turned it upside down in the bath of mercury. Then I dissolved 21 g of pure potassium hydroxide in 66 g of water. I took two equal volumes of this solution, one of which I introduced into the jar and the other into a second jar filled with mercury. I left the first jar in front of a burning oven for thirty hours while agitating the contents from time to time. I noticed the evolution of bubbles of gas that collected in the top of the vessel¹⁰. When the saponification was complete, I introduced into the jar with the pure caustic potash an amount of concentrated hydrochloric acid that was slightly more than sufficient to neutralize the alkali. This led to the release of 30 mL of carbon dioxide. Having thus determined the amount of this gas present in the potash used for the saponification, I transferred the mother liquor of the soap into a much larger jar than the original one, since I feared that the latter would be too small to contain

* It could also be that the acid that I regard here as acetic acid only resembled it with respect to volatility and odor and that it in fact belongs to the group of volatile acids that I described in Book II. In that case, it originates from an oil that is similar to butyryl, and the phocenin present in lard.

all the carbon dioxide that could be produced. After the transfer, I acidulated the soap with the same amount of hydrochloric acid as used in the previous experiment. The acidulation took a long time because there was little contact between the acid and the soap. When it had finally been completed, the acidulation products were combined with the mother liquor and the gaseous product was separated and analyzed by means of potash. It consisted of 31 mL of carbon dioxide and 5.57 mL of a gas that had the properties of nitrogen since it did not sustain combustion, was non-flammable and insoluble in water and potash. I think that this experiment allows us to conclude that no significant amount of carbon dioxide is produced during the saponification of lard.

969. Human fat, jaguar fat, beef and mutton tallow gave the same result, as shown in the table below:

		ALKALI	
		USED FOR SAPONIFICATION	USED AS REFERENCE
20 gram of human fat	Amount <i>a</i> of carbon dioxide		Amount <i>a</i> of carbon dioxide + 5 mL
20 gram of jaguar fat	Amount <i>a</i> of carbon dioxide		Amount <i>a</i> of carbon dioxide
20 gram of beef tallow	Amount <i>a</i> of carbon dioxide +5 mL		Amount <i>a</i> of carbon dioxide
20 gram of mutton tallow	Amount <i>a</i> of carbon dioxide		Amount <i>a</i> of carbon dioxide + 4.5 mL

970. The first column shows the amount and the name of the fat saponified. The second and the third columns indicate whether or not there was a difference between the volume of carbon dioxide that was obtained from the alkali that was used to saponify the fat and the volume of carbon dioxide obtained from the same amount of reference alkali that was not used for saponification. Where there was a difference, the excess amount of carbon dioxide has been given in mL¹¹.

971. Butterfat and fish oil were saponified without producing carbon dioxide.

972. An amount of 3.10 g of spermaceti was melted in a bell jar. When it had solidified, the jar was filled with mercury and placed upside down in a bath of this metal. A strong solution of potassium hydroxide containing about 5 g of alkali was boiled for a long time to drive out the air and then added to the bath. An equal volume of this solution was set aside. The spermaceti was heated every day for a month, after which saponification appeared to be complete and no noticeable amount of gas had been released. Hydrochloric acid was introduced into the jar and when the acidulation of the soap was complete, an amount of carbon dioxide was obtained that after rigorous drying had a volume of 30 mL at a temperature of zero degrees and a pressure of 760 mmHg. The

potassium hydroxide solution with a volume equal to that of the solution that had been used for the saponification was then supersaturated with the same amount of hydrochloric acid. It yielded 21 mL of carbon dioxide. Therefore, there was an excess of 9 mL of this gas weighing 17.8 mg in the caustic potash that had saponified the spermaceti. In other words, 100 parts of spermaceti would yield only 0.57 parts carbon dioxide. I consider this amount to be too small to be taken into account.

§ 3. IS OXYGEN NECESSARY FOR SAPONIFICATION ?

973. Although this question has been answered almost completely by the previous experiments, I think I must report the following experiment, which has been carried out with much care. While taking the precautions indicated above, I placed 50 g of fat that had been kept molten for some time in a jar with a volume of 3 dL containing some mercury. I turned the jar upside down in a bath of mercury. Then I started boiling 250 g of water¹² and when about 100 g had evaporated, I allowed the residue to cool on top of the mercury, without contact with air. I made a solution of 30 g pure potassium hydroxide and introduced this solution into the jar containing the fat. The materials were placed between two ovens that were kept burning for three days. At first, the fat became opaque and gelatinous; it looked like congealed oil. Gradually, the gelatinous mass grew in size and at the same time, it lost its opacity. During the reaction, only a few gas bubbles evolved. When the process appeared to have finished, the materials were left to stand. After two weeks, star-shaped crystals had formed in the gelatinous mass. Gradually their number increased to such an extent that the soap seemed to consist entirely thereof. These crystals were potassium palmitate and potassium stearate. After three months, the soapy mass was heated and two thirds of it were introduced into a 4 dL jar full of mercury. Then the two portions of soap were acidulated with hydrochloric acid and the gases originating from the acidulation of the soap were collected. Removal of the carbon dioxide from the gases left 3.80 mL of nitrogen. It follows from this experiment that: 1. saponification takes place without contact with oxygen gas; 2. that potassium palmitate and stearate can precipitate spontaneously from soap without the intervention of any substances other than those that were utilized for the saponification. The only condition to be met for this precipitation to take place is that enough water is used to cause the soap to be gelatinous and thereby reduce the affinity of potassium oleate for potassium palmitate and potassium stearate; 3. that the nitrogen gas that is released when the potash reacts with the fat is incidental since in the experiment that I have just described, where more stringent measures were taken to expel all the air from the reagents than in experiment (972), the amount of gas obtained was far from proportional to the amount obtained in experiment (972).

974. Since I said that a small amount of air was present in the experiments I have just described and that the nitrogen seems to have been separated from the oxygen, it could be concluded that the latter is necessary for saponification to take place. But is it likely that such a small amount of oxygen would have any effect? And since the two experiments produced soaps that were equally well saponified, would it not be absurd to believe that two totally different amounts of oxygen could have given the same result? I think that the oxygen was absorbed by only part of the fat, just as it has been observed that only parts of a fatty matter turn rancid in an atmosphere that does not contain enough oxygen for the entire amount to become rancid.

¹ Georg Ernst Stahl (1660-1734) was a disciple of Johann Joachim Becher (1635-1682), who introduced the phlogiston theory that was further developed by Stahl.

² Claude Louis Berthollet (1748-1822) is best known for his work on chlorine. He prepared hypochlorite bleaches and discovered chlorates.

³ Hans Christian Ørsted (1777-1851) was a Danish scientist who was the first to produce metallic aluminum (1825) from aluminum chloride and potassium metal. His main contributions to science concern electromagnetism. In 1930, the unit of magnetic field strength (oe, Ampère/m) was named after him

⁴ Here the author takes a sideswipe at Fourcroy whom he disliked and found haughty and pompous (A.B. Costa, *Michel Eugène Chevreul and the Chemistry of Fatty Oils*, Ph.D. Thesis, University of Wisconsin, Madison, 1960, page 5).

⁵ These are the books in the present monograph.

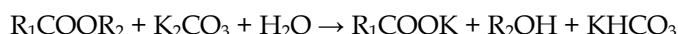
⁶ Just like § 3 in Chapter 4 of the previous Book, this chapter has no title either.

⁷ The process of manufacturing pure potassium hydroxide by extraction with alcohol has been explained in the foreword on page xxviii. In the present sub-section he compares potassium hydroxide made by the alcohol extraction process with potassium hydroxide that has been manufactured without such an extraction. Accordingly, two different terms are needed. I have therefore introduced the term 'alcoholic' potassium hydroxide but only for the present sub-section. Elsewhere the term 'pure potassium hydroxide' is used.

⁸ See endnote 4 on page 205.

⁹ This centigram is the 10 mg mentioned four lines above.

¹⁰ This gas is probably air since the saponification reaction:



does not release any carbon dioxide. This gas is only released when the soaps are acidulated and the acid used also reacts with the potassium hydrogen carbonate formed during saponification and the residual potash that was used in excess.

¹¹ The original uses cubic centimetres but for the sake of internal consistency, volumes are quoted in liters and their multiples.

¹² Presumably, the water was boiled to expel all the oxygen.