Saponification

From Wikipedia, the free encyclopedia

Saponification is a process that produces soap, usually from fats and lye.[1]

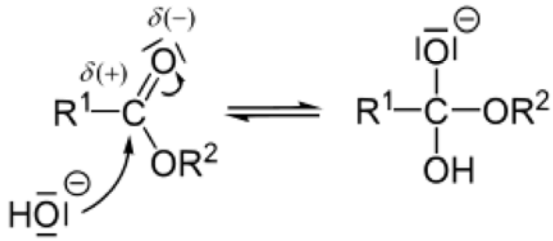
Contents

Triglycerides

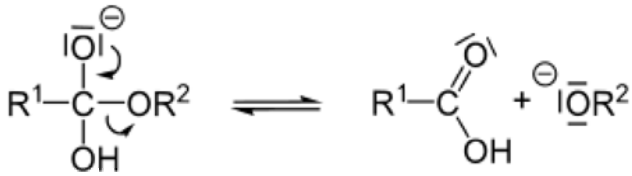
Vegetable oils and animal fats are the main materials that are saponified. These greasy materials, triesters called triglycerides, are mixtures derived from diverse fatty acids. Triglycerides can be converted to soap in either a one- or a two-step process. In the traditional one-step process, the triglyceride is treated with a strong base (e.g., lye), which accelerates cleavage of the ester bond and releases the fatty acid salt and glycerol. This process is the main industrial method for producing glycerol. If necessary, soaps may be precipitated by salting it out with saturated sodium chloride. The saponification value is the amount of base required to saponify a fat sample. For soap making, the triglycerides are highly purified, but saponification includes other base hydrolysis of unpurified triglycerides, for example, the conversion of the fat of a corpse into adipocere, often called "grave wax." This process is more common where the amount of fatty tissue is high, the agents of decomposition are absent or only minutely present.

Mechanism of base hydrolysis

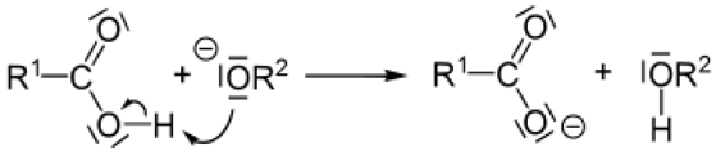
The mechanism by which esters are cleaved by base involves a series of equilibria.[2] The hydroxide anion adds to (or "attacks") the carbonyl group of the ester. The immediate product is called an orthoester:



Expulsion of the alkoxide generates a carboxylic acid:



The alkoxide ion is a strong base so that the proton is transferred from the carboxylic acid to the alkoxide ion creating an alcohol:



In a classic laboratory procedure, the triglyceride trimyristin is obtained by extracting it from nutmeg with diethyl ether.[3] Saponification to the sodium salt of myristic acid takes place with NaOH in water. The acid itself can be obtained by adding dilute hydrochloric acid.[4]

Steam hydrolysis

Triglycerides are also saponified in a two-step process that begins with steam hydrolysis of the triglyceride. This process gives the carboxylic acid, not its salt, as well as glycerol. Subsequently, the fatty acid is neutralized with alkali to give the soap. The advantage of the two-step process is that the fatty acids can be purified, which leads to soaps of improved quality. Steam hydrolysis proceeds via a mechanism similar to the base-catalyzed route, involving the attack of water (not hydroxide) at the carbonyl center. The process is slower, hence steam is required .

Applications

Soft versus hard soap

Depending on the nature of the alkali used in their production, soaps have distinct properties. Sodium hydroxide (NaOH) gives "hard soap"; hard soaps can also be used in water containing Mg, Cl, and Ca salts. By contrast, when potassium hydroxide (KOH) is used, a soft soap is formed.

Lithium soaps

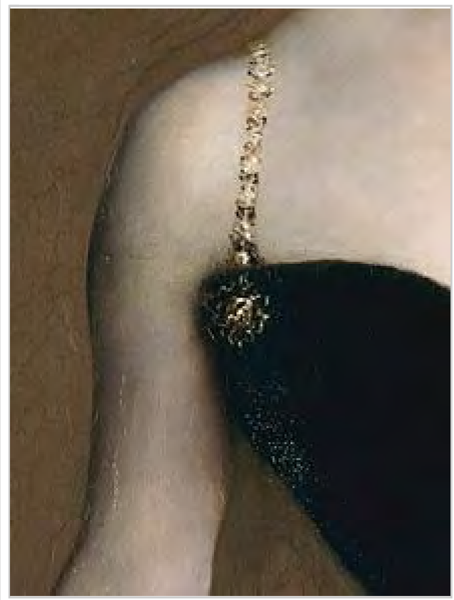
Lithium derivatives of 12-hydroxystearate and several other carboxylic acids are important constituents of lubricating greases. In lithium-based greases, lithium carboxylates are thickeners. "Complex soaps" are also common, these being combinations of metallic soaps, such as lithium and calcium soaps.[5]

Fire extinguishers

Fires involving cooking fats and oils (classified as class K (US) or F (Australia/Europe/Asia)) burn hotter than flammable liquids, rendering a standard class B extinguisher ineffective. Flammable liquids have flash points under 37 degrees Celsius. Cooking oil is a combustible liquid, since it has a flash point over 37 degrees Celsius. Such fires should be extinguished with a wet chemical extinguisher. Extinguishers of this type are designed to extinguish cooking fats and oils through saponification. The extinguishing agent rapidly converts the burning substance to a non-combustible soap. This process is endothermic, meaning that it absorbs thermal energy from its surroundings, which decreases the temperature of the surroundings, further inhibiting the fire.

Oil paints

Saponification can occur in oil paintings over time, causing visible damage and deformation. The ground layer or paint layers of oil paintings commonly contain heavy metals in pigments such as lead white, red lead, or zinc white. If those heavy metals react with free fatty acids in the oil medium that binds the pigments together, soaps may form in a paint layer that can then migrate outward to the painting's surface.[6]



Detail of Madame X (Madame Pierre Gautreau), John Singer Sargent, 1884, showing saponification in the black dress.

Saponification in oil paintings was described as early as 1912.[7] It is believed to be widespread, having been observed in many works dating from the fifteenth through the twentieth centuries, works of different geographic origin, and works painted on various supports, such as canvas, paper, wood, and copper. Chemical analysis may reveal saponification occurring in a painting’s deeper layers before any signs are visible on the surface, even in paintings centuries old.[8]

The saponified regions may deform the painting's surface through the formation of visible lumps or protrusions that can scatter light. These soap lumps may be prominent only on certain regions of the painting rather than throughout. In John Singer Sargent’s famous *Portrait of Madame X*, for example, the lumps only appear on the blackest areas, which may be because of the artist’s use of more medium in those areas to compensate for the tendency of black pigments to soak it up.[9] The process can also form chalky white deposits on a painting’s surface, a deformation often described as "blooming" or "efflorescence," and may also contribute to the increased transparency of certain paint layers within an oil painting over time.[10]

The process is still not fully understood. Saponification does not occur in all oil paintings containing the right materials. It is not yet known what triggers the process, what makes it worse, or whether it can be halted.[11] At present, retouching is the only known restoration method.

See also

- Soap
- Unsaponifiable
- Adipocere

References

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7. Fleury, Paul (1912). "MANUFACTURE AND TREATMENTS OF WHITE ZINC". *The Preparation and Uses of White Zinc Paints* (1st ed.). London: London, Scott, Greenwood & son. "and although Petit declares this theory false, it is none the less on it and on its data that he bases his system of manufacture of hydrated white zinc, of which he is the inventor that is to say, the saponification of the oil, or the formation of metallic salts, dissolved therein"
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9. Silvia A. Centeno; Dorothy Mahon (Summer 2009). Macro Leona, ed. "The Chemistry of Aging in Oil Paintings: Metal Soaps and Visual Changes". *The Metropolitan Museum of Art Bulletin*. Metropolitan Museum of Art. **67** (1): 12–19. JSTOR 40588562. See pages 12–13, 15.
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External links

- Animation of the mechanism of base hydrolysis (https://commons.wikimedia.org/wiki/File%3AVerseifung_startAnimGif.gif)

Categories: Substitution reactions | Chemical processes | Soaps | Bases (chemistry) | Conservation and restoration of paintings

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