Revisiting the mechanisms of low-temperature, base-catalysed ester interchange reactions

Albert J. DIJKSTRA

Carbougnères, F-47210 St. Eutrope-de-Born
<albert@dijkstra-tucker.be>

Abstract: *Ester interchange reactions such as the interesterification of triglycerides and their transesterification with methanol (methanolysis) to produce FAME (biodiesel) nowadays invariably use a basic catalyst such as an alkali alcoholate or hydroxide. Whereas it was formerly assumed that the catalytically active intermediates in the interesterification reaction and the methanolysis reaction were the glycerolate anion and the methanolate anion respectively, it now looks far more likely that the enolate anion plays a major role whenever the concentration of free alcohol groups in the reaction medium is small in comparison with the concentration of fatty acid moieties. Which mechanism dominates in which reaction and which reaction stage will be explained and discussed.*

Key words: *ester interchange, interesterification, transesterification, mechanism*

Introduction

In the middle of the 19th century, both the alkali catalysed alcoholysis reaction [1] and the temperature induced ester interchange reaction [2] were discovered. They are both examples of reactions whereby an ester made from a carboxylic acid and an alcohol reacts to form a different ester. If the ester reacts with a different carboxylic acid, the ester interchange reaction is called *acidolysis*, if it reacts with an alcohol it is called *alcoholysis* or more specifically *methanolysis, ethanolysis, glycerolysis*, etc. and when the ester reacts with another ester, the term *interesterification* is generally used. However, this nomenclature is not universally in force. The conversion of triglycerides into biodiesel is called a *transesterification* and the divalent metal catalysed reaction between dimethyl terephthalate (DMT) and ethylene glycol (ethanediol) is generally referred to as *ester interchange* rather than *glycolysis;* the subsequent distillative removal of the excess of ethylene glycol to produce polyester polymer is not called an *interesterification* but a *polycondensation*.

Ester interchange reactions are carried out over a wide temperature range and employ a great number of different acids, alcohols and catalysts. However, the present paper will be limited to ester interchange reactions between esters of fatty acids that are base-catalysed and proceed at temperatures below 100°C. These reactions are gaining in industrial importance for two reasons: The current *trans* fatty acid scare has led to a shift from partial hydrogenation to interesterification of highly saturated triglycerides with lower melting triglycerides (such as lauric oil or liquid oils) and secondly, the political decision to subsidise biodiesel has caused its installed production capacity to increase at an alarming rate.

For these low temperature ester interchange processes, several basic catalysts have been proposed. Such a catalyst was for instance disclosed by Normann [3], who used sodium ethanolate but did so at temperatures in excess of 200 °C. Naudet used sodium methanolate [4] for the work that led to his doctoral thesis and also employed high temperatures. Eckey started by using high temperatures and found that just water could cause interesterification by a process of hydrolysis followed by esterification [5] but subsequently, when he invented directed interesterification based on the crystallisation of the triglycerides with the highest melting point [6], he uses catalysts such as alkali metal alcoholates that are active at low temperature. He remarks: "It is not unlikely that the true catalyst for the rearrangement reaction is not the alkoxide or other compound added to the triglyceride, but rather a compound resulting from the reaction of such added compound with the triglyceride fat. For example, I have observed that almost immediately after the introduction of sodium methoxide into a fat there is formed substantially an equivalent amount of fatty acid methyl ester. It is the logical assumption therefore, that the sodium has combined with the triglyceride fat in some form, and according to my theory this sodium-fat compound constitutes the active catalyst constituent in this particular instance."

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Early mechanisms

It was not until 1960 that Baltes [7] proposed that this "active catalyst constituent" could well be the glycerolate anion. He suggested that this be formed by the reaction of the sodium methanolate anion with a triacylglycerol molecule according to *figure 1*.

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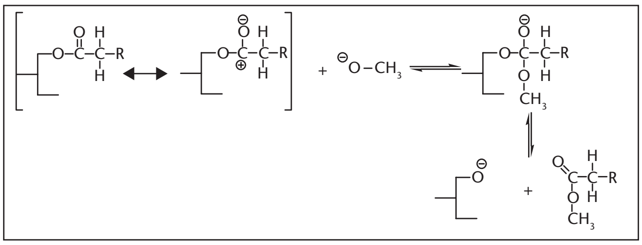

Figure 1. *Formation of the glycerolate anion.*

Subsequently, this glycerolate anion can react with triglycerides and cause an interesterification reaction according to *figure 2*.

Formation of an enolate anion

At about the same time as Baltes [7] suggested his mechanism, Weiss *et al.* [8] suggested a different mechanism whereby in a first step an enolate anion is formed according to *figure 3*.

Subsequently, this enolate anion reacts further with a fatty acid moiety to form a β-keto ester, which they considered to be the "active catalytic constituent" *(figure 4)*.

However, the fact that this β-keto ester was formed only gradually [9] and that the infra red absorption spectrum presumed to be indicative of this ester could also be explained by the absorption characteristics of soaps [10] caused the glycerolate mechanism proposed by Baltes [7] to be generally accepted. It was also supported kinetically by Steenhoek [11, 12] but support is not the same as proof.

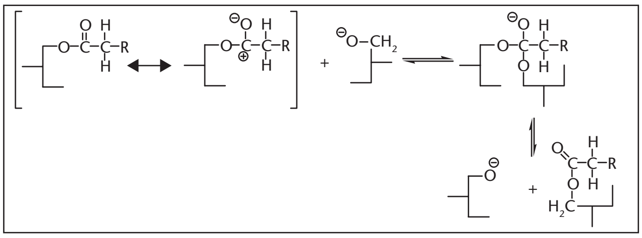

Figure 2. *Glycerolate catalysed interestification of triglycerides.*

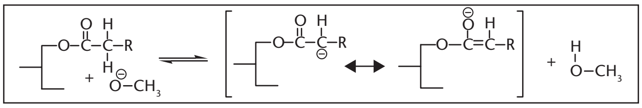

Figure 3. *Enolate anion formation by abstraction of an α-hyrdrogen by a methanolate anion.*

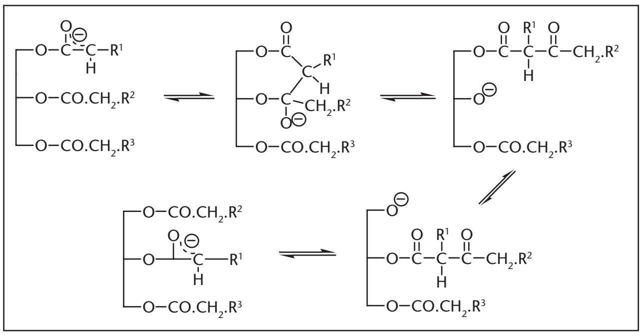

Figure 4. *The enolate anion reacts with a fatty acid moiety to form a β-keto ester.*

In 2004, Liu [13] asked how the chemical interesterification is initiated: by a nucleophilic substitution or by the abstraction of an α-proton? By observing that α-substituted fatty acids did not participate in ester-ester interchange on the addition of sodium methanolate and only formed methyl esters on the subsequent addition of methanol, Liu [13] concluded that the first step in the methanolate catalysed interesterification is the abstraction of an α-hydrogen from a fatty acid moiety to form an enolate carbanion. He then assumed the interesterification to be completed via a Claisen condensation mechanism involving the β-keto ester as the active intermediate.

The "enolate" mechanism

Besides the observation by Liu [13] that without an α-hydrogen, there is no ester interchange, which observation cannot be explained by the glycerolate mechanism, further objections against the glycerolate mechanism were put forward [14]: it does not explain why an amount of soap or FFA is formed that is equivalent to the amount of sodium methanolate catalyst used, and it does not explain why compounds like acetone [15] or "an aprotic substance selected from the group consisting of dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide, dimethyl cyanaminde, 3,3-dimethylaminopropionitrile, and mixtures thereof" [16] accelerate the ester interchange reaction.

According to Seestrom *et al.* [17] an equivalent amount of soap or FFA is formed during interesterification according to:

2 triglycerides + 1 sodium methoxide → 1 soap + 1 methyl esters + 2 diglycerides

This observation has been confirmed independently by several authors and also forms the basis of cost comparisons [18, p. 155].

This formation is explained by Rozendaal [19, 20] by assuming a quantitative saponification reaction between the sodium hydroxide formed on inactivation of the catalyst (the sodium glycerolate anion) and triglycerides present but given the rate constant of this saponification reaction, this is highly unlikely. When acidified water is used for catalyst inactivation, the assumption that the caustic soda formed by the inactivation reaction first of all saponifies a glyceride and that the soap thus formed is acidulated and yields a free fatty acid is even less likely, if not impossible.

Accordingly, Dijkstra [14] proposed a mechanism that assumes that the enolate anion is the active catalytic constituent [21]. It is formed by the abstraction of an α-proton as indicated above and subsequently, it reacts with hydroxyl groups. If this hydroxyl group belongs to an alcohol, this leads to alcoholysis as illustrated *figure 5* for methanol.

If this hydroxyl group forms part of a partial glyceride, the result of the reaction is an ester interchange *(figure 6)*, and if the hydroxyl group is part of a water molecule, the reaction leads to catalyst inactivation and the formation of a free fatty acid moiety according to *figure 7*.

As shown above, the reactions between the enolate anion and the alcohol or partial glyceride lead to the formation of the glycerolate anion but according to the theory put forward by Dijkstra *et al.* [21], this glycerolate anion will abstract an α-proton from a fatty acid moiety and thereby regenerate the active catalytic constituent. There are two reasons for this regeneration reaction. The first one is thermodynamic. Because of

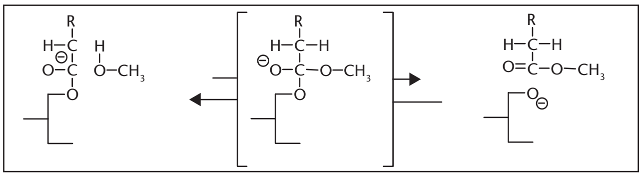

Figure 5. *Alcoholysis with enolate anion as catalytically active intermiediate.*

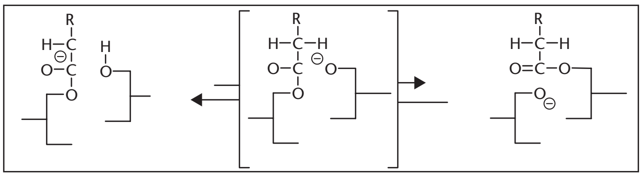

Figure 6. *The reaction as an ester interchange if the hydroxyl group forms part of a partial glyceride.*

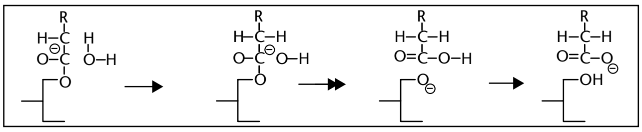

Figure 7. *The formation of a free fatty acid moiety if the hydroxyl group is part of a water molecule.*

its stabilisation by resonance, the enolate anion is favoured over the glycerolate anion and certainly over the methanolate anion. The second, kinetic reason is especially important in the interesterification of triglycerides where the concentration of fatty acid moieties is much higher than the concentration of free hydroxyl groups. Moreover, the experimental observation that there is an equivalent liberation of free fatty acid moieties when the catalyst is inactivated by water also points to the equilibrium between the glycerolate anion and the enolate anion to be far to the enolate side.

In order to explain the loss of catalytic activity when the temperature is raised above 100 °C, Dijkstra [14] suggested that the enolate anion reacts with a fatty acid moiety to form a β-keto ester in accordance with the proposal by Weiss *et al.* [8]. This suggestion is in line with the observation [9] that it is formed gradually. He further suggested that this β-keto ester had no catalytic activity.

Finally, Dijkstra [14] provided an explanation for the accelerating effect of acetone [15] and aprotic substances listed above [16]. He suggested that compounds like acetone act as proton transfer agents and thereby accelerate the regeneration of the enolate anion by the glycerolate anion according to *figure 8*.

The above reaction has been demonstrated experimentally [21]. By adding a small amount (2%) of acetone-d_6 to an interesterification mixture of trilaurin and triolein and analysing samples taken at regular intervals by ^{2}H-NMR spectroscopy, a chemical shift of the signal observed was found to correspond to the expected value of a C-D bond at the α-position of the ester. In addition it was once again shown that acetone accelerates the interesterification reaction. This demonstration provides independent support for the enolate mechanism.

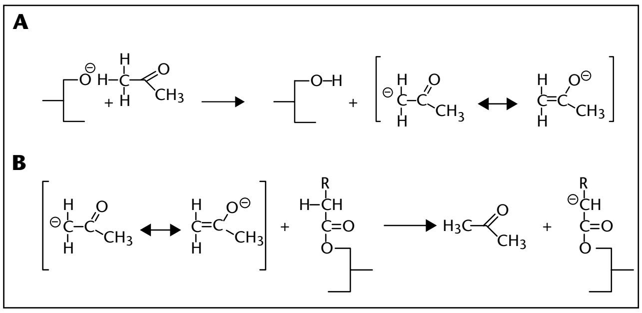

Figure 8. *The accelerating effect of acetone. A) Acetone acts as proton transfer agent. B) Accelerates the regeneration of the enolate anion by the glycerolate anion.*

What happens in industrial processes

In the domain of edible oils and fats, the two industrial processes involving low-temperature, base-catalysed ester interchange reactions are the interesterification between triglycerides and the transesterification of triglycerides with methanol to produce FAME. Glycerolysis of triglycerides to produce monoglycerides is not carried out at low temperatures because of the poor solubility of glycerol in the reaction medium. Given the ester interchange equilibria between triglycerides, diglycerides, monoglycerides and glycerol, a high conversion to monoglycerides can only result when the glycerol concentration is high [22].

When triglycerides are interesterified using sodium methanolate as basic catalyst, an amount of 0.05 % by weight suffices, provided the oil is dry and neutral. In the literature [e.g. 11], it is generally assumed that this methanolate will react with a triglyceride to form a glycerolate anion and a FAME molecule as shown in *figure 1*. However, for thermodynamic reasons it is more likely that at least a substantial part of the methanolate will react with fatty acid moieties by abstracting an α-proton and form an enolate anion and free methanol according to *figure 3*. This free methanol will then eventually meet an enolate anion and form a FAME and a glycerolate anion according to *figure 5* that in its turn regenerates the enolate anion. The above explains why methanol, when added to an interesterification mixture of triglycerides, ends up quantitatively as FAME [6], an observation that is not easily explained by assuming that only methanolate anions can form FAME.

FAME formation can be avoided by using another catalyst such as for example alkali metals. There are sodium/potassium alloys that are liquid at room temperature [23] and they can be easily dispersed in the oil [24]. Such alloys have been profitably used in directed esterification processes [25] by dispersing the alloy in the oil, heating the oil until a colour change was observed indicating that the catalyst was ‘activated’. Subsequent cooling causes high melting triglycerides to crystallise and provide some consistency to the resulting fat blend.

The discolouration on catalyst activation has been reported to be due to the presence of oxidation products [26]. Much later, it has been suggested to use this colour formation as a means to control the extent of the interesterification reaction [27, 28] but the merits of this method of control have been shown to be spurious, since partially interesterified products can be made more reproducibly and more cheaply by mixing fully randomised products with their raw materials [29].

In interesterification reaction mixtures, the concentration of fatty acid moieties is very much higher than the concentration of free hydroxyl groups. On the other hand, when triglycerides are transesterified with methanol to produce FAME, the concentrations of these groups differ far less. Moreover, the reaction is complicated by the fact that in the beginning, not all methanol dissolves in the oil and at the end, glycerol forms a separate phase. In the diagram *figure 9*, the equilibria between

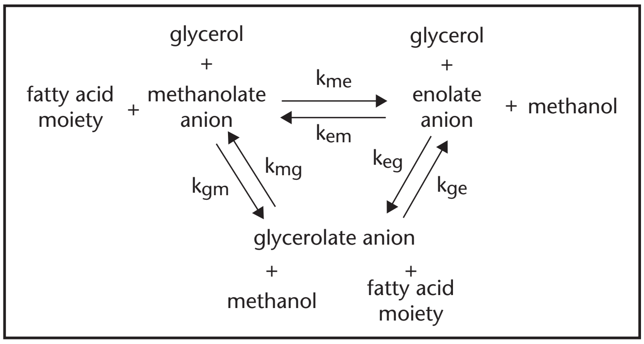

Figure 9. *The equilibria between the various anions.*

the various anions have been depicted.

In this diagram, the arrows have been drawn at different thickness to indicate that energetically, the enolate anion is favoured over the methanolate anion as well as over the glycerolate anion and that the glycerolate anion is favoured over the methanolate anion. However, kinetic factors and solubilities also play a considerable role. In case of the methanolate catalysed transesterification of triglycerides with methanol, the catalyst will originally be concentrated in the polar methanol phase and the predominant anion will therefore be the methanolate anion. Since some methanol will dissolve in the oil phase, some catalyst will also be present in this oil phase. Since the concentration of fatty acid moieties in this oil phase is much higher than the methanol concentration and since the enolate anion is energetically favoured over the methanolate anion, the predominant anion in the oil phase will be the enolate anion. This anion will react with methanol so that FAME are formed and the glycerolate anions formed simultaneously will regenerate enolate anions rather than form methanolate anions.

When the concentration of glycerolic hydroxyl groups in the oil phase gradually increases by the formation of partial glycerides, the solubility of the methanol in the oil phase also increases so that eventually, the original two-phase system becomes a one-phase system; then all the catalyst is dissolved in this single phase but it is unlikely to be a single catalyst. In that single phase, there will be many fatty acid ester moieties so there is ample opportunity for the enolate anions to be present since they are also energetically favoured. The FAME present in the reaction mixture will also form enolate anions and although they do not contribute to the progress of the transesterification reaction, they may well capture a substantial proportion of the total alkalinity in the reaction mixture and thereby decrease the rate of conversion of methanol to FAME.

As and when the methanol concentration decreases, the methanolate anion concentration will also decrease and the increasing concentration of glycerolic hydroxyl groups will cause the glycerolate anion concentration to increase. At a certain stage, free glycerol will have been formed and when its concentration exceeds its solubility in the oily reaction mixture, a separate, glycerol phase will be formed and this phase will grow when more free glycerol becomes available. Moreover, its solubility in the oil phase will also decrease when the partial glyceride content in this phase decreases and this will also cause the glycerol phase to grow.

With the emergence of a separate glycerol phase, the various constituents will divide themselves over the two phases and equilibria between anions will also shift. The glycerides will be strongly concentrated in the FAME phase that will contain less and less glycerol when the glycerol hydroxyl group content decreases further. The methanol will have a preference for the glycerol phase but since the glycerol phase will be only about one tenth of the FAME phase, the major part of the methanol will still reside in the FAME phase.

What about the anions? At the end of the transesterification reaction, titration shows the FAME phase to be alkaline but less so than the glycerol phase. Accordingly, the anions present in the FAME phase will be predominantly enolate anions with some methanolate anions. In the glycerol phase, they will be predominantly glycerolate anions again with some methanolate anions.

Not all industrial transesterification processes use sodium methanolate as ester interchange catalyst. Some use sodium hydroxide or potassium hydroxide. This use introduces a further anion into the system: the hydroxyl anion. It also raises the question how this further anion will affect the concentrations of the other anions. Energetically, the hydroxyl anion is the most favoured. Water will react with the methanolate anion to form the hydroxyl anion and methanol. Glycerolate will react with water to form the hydroxyl anion and glycerol and as illustrated previously *(figure 7)*, the enolate anion also reacts with water to finally give a fatty acid anion and a partial glyceride.

However, the positions of the various equilibria depend strongly on the concentrations of the reactants involved. As pointed out by Mittelbach and Remschmidt (See page 51 in [30]), the use of alkali hydroxides as transesterification catalysts entails the presence of so little water that it will affect the concentration of the various anions only to a small extent. Moreover, these authors [30] also claim that the low concentration of hydroxyl anions in the FAME phase also slows down the formation of soap.

So far, the discussion has been limited to the various anions but could the cations also affect the interesterification and transesterification reactions? Very little has been published about this. Baltes [7, 31] relates catalytic activity to the electropositive character of the cation and lists these cations in order of decreasing activity as: K-Na-Li-Mg-Zn. This order has also been mentioned by the German Working Party [32] but since then, no studies have been published on this particular subject.

Discussion

In addition to the sodium methanolate and alkali metal catalysts mentioned above, the literature [10] also mentions sodium amide [33] and sodium hydride [34] but it is doubtful if they have ever been used industrially. Their action has always been assumed to lead to the same glycerolate anions as do the sodium methanolate and sodium metal and in the light of the above, they can be assumed to lead to the same enolate anions during interesterification and to the same enolate, glycerolate and methanolate anions during the transesterification.

When sodium hydroxide is dissolved in glycerol and dried under vacuum [35, 36], it cannot but form sodium glycerolate. If this sodium glycerolate is then used as interesterification catalyst and mixed with oil, the glycerolate anion is likely to react with fatty acid moieties and form an enolate anion which, given the elevated temperature (160 to 190 °C) may then react to form the catalytically inactive β-keto ester. This raises the question what catalytically active intermediate operates at these high temperatures. From the work by Naudet [4] it is known that this intermediate is not very active, so perhaps, the β-keto ester still has some catalytic activity left as suggested by Weiss *et al.* [8]. Since the interesterification occurs spontaneously at somewhat higher temperatures, not much catalytic activity is required anyway.

However, this is pure speculation and the fact that speculation is required illustrates that not enough research has been devoted to the elucidation of the high-temperature mechanism of the ester interchange reaction. In this respect, this reaction is not unique. Sadly enough, there are quite few reactions and processes In the edible oils and fats industry, that are poorly understood as a consequence of which potential savings are not being realised.

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