



Investigation of the electrosynthetic pathway of the aldol condensation of acetone



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HIGHLIGHTS

- The potential-controlled aldol condensation of acetone to diacetone alcohol is performed.
- Additional water in the electrolyte has a disadvantageous effect on the reaction.
- The concentration increase of diacetone alcohol describes an exponential curve.

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ABSTRACT

The potential-controlled electrochemical aldol condensation of acetone to diacetone alcohol in a standard batch electrolysis set-up was studied in this work. It is confirmed that the reaction proceeds at the cathode and that, contrary to what is mentioned in earlier literature, water in the electrolyte has a disadvantageous effect on the reaction. Similar to the chemical reaction, the electrochemical reaction reaches a maximum yield when the equilibrium is reached. Separating the anode and cathode prevents cross-over and degradation of products, leading to a higher yield. Starting with pure acetone and support electrolyte, it was possible to obtain a diacetone alcohol concentration of 15 mM after 2 h electrolysis in a divided set-up with a platinum electrode at -2.5 V. The concentration gradient throughout the electrolysis follows an exponential curve up to its equilibrium concentration.

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1. Introduction

Acetone is the starting material to a broad range of products and intermediates [1,2]. The aldol condensation of acetone initially produces 4-hydroxy-4-methyl-pentan-2-one, commonly known as diacetone alcohol (DAA) (see Fig. 1). Diacetone alcohol is an industrially useful and important product with a number of applications. It is used as a solvent in varnishes, paints, cellulose acetate lacquer, thinners and in cleaning compounds and is considered to be an environmentally friendly alternative to other materials such as acetone due to its much lower volatility [3]. It is also an intermediate to other industrially important products. The dehydration of diacetone alcohol yields mesityl oxide, a useful compound with various applications, but primarily it is the precursor of methyl isobutyl ketone (MIBK), a popular solvent used mainly in the paint

and coating industry [4] and the largest volume aldol reaction product of acetone [2]. Heavier products from acetone such as phorone, isophorone and 3,5-xyleneol are formed by self-condensation or cross-condensation between the same or different ketones that are formed in the reaction and also find many applications. To optimise the yield of the desired product DAA, further condensation reactions have to be prevented without shifting the equilibrium towards the dehydration product mesityl oxide. A high-performance catalyst which not only gives high DAA yields, but also a high selectivity is required and thus, much attention has been given to the catalyst.

Conventionally, the aldol condensation of acetone is conducted using a homogeneous base catalyst such as NaOH and KOH [2,5]. Some major drawbacks are associated with the homogeneity and basic nature of the catalysts. The strong bases require specific measures to prevent corrosion problems which leads to high capital costs. The homogeneity of the catalyst requires intense purification afterwards in which the catalyst often is destroyed. In the conventional process, phosphoric acid is added to neutralise the catalyst and stabilize DAA, after which DAA is recovered by evaporation

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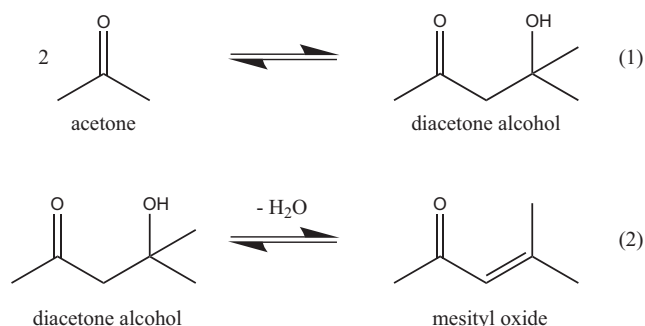


Fig. 1. Aldol addition of acetone to diacetone alcohol (1) and dehydration of diacetone alcohol to mesityl oxide (2) to complete the aldol condensation. Reaction 1 is of interest in this work.

Table 1
Equilibrium conversions of acetone to DAA [10].

Temperature (°C)	0	10	20	30
Conversion (wt%)	23.1	16.9	12.1	9.1

and stripping of the acetone, which is then recycled [1,6]. This neutralisation step must be accurately controlled as an excess of acid causes facile dehydration of DAA to MO [7]. The neutralisation process and subsequent purification steps by distillation entail a high cost and produce large amounts of waste streams. It has been estimated for these compounds that product purification, recovery and waste treatment account for 30% of the selling price [8].

Because of the disadvantages inherent to the homogeneous catalysts, heterogeneous systems offer a viable alternative. Solid acid-base catalysts are becoming increasingly important in chemical and life science industry as they have many advantages over homogeneous liquid acid-base catalysts [8,9]. Separation of the product stream is much easier, reducing purification costs and increasing catalyst life. They are more environmentally friendly than the homogeneous catalysts and are non-corrosive, making safe handling and disposal easier. Zeolites, oxides and ionic exchange resins make up about 80% of the types of solid acid-base catalysts used in industrial processes while dehydration and condensation reactions most often use these types of catalysts [9]. Some commercial installations for the production of DAA use fixed-bed reactors employing solid alkaline catalysts such as Ba(OH)₂ and Ca(OH)₂. However, self-condensation of acetone to diacetone alcohol is a reversible exothermic reaction which is equilibrium limited with the equilibrium strongly favouring acetone. (see Table 1). To obtain a reasonable yield, commercial operations are conducted at 10–20 °C with typical residence times of 20–60 min. A lower temperature has a favourable effect on the equilibrium of the reaction, but results in slower kinetics, giving a maximum possible conversion of acetone of 15% per pass at 15 °C [6]. Furthermore, many of the catalysts are susceptible to alkali dissolution and end up in the product stream.

To meet the requirements of the toughening environmental regulations and economical demands of the industry, lots of attention has been focused on improving the catalyst of the reaction to increase the yield of diacetone alcohol or mesityl oxide. Different types of basic catalysts have been proposed for the condensation of acetone to diacetone alcohol, such as metal hydroxides [11,12], metal oxides [11,13–16] promoted with alkali or alkaline earth metal ions [17], mixed metal oxides [18,19], layered double hydroxides [20,21] and anionic and cationic exchange membranes [22–25]. Besides improving the catalyst, some research also focuses on a different reaction technique instead of conventional batch reactors or fixed-bed reactors, such as catalytic distillation

[16,23–26]. Nicol [24] concluded that catalytic distillation is the inferior option compared with the conventional separate reaction and distillation process for DAA production, Podrebarac et al. [23] came to a similar conclusion. Both mention factors attributed to the catalyst as the main cause, which is also concluded by Huang et al. [27]. Nicol further notes that the decoupled temperature and pressure dependence in the conventional process is a major advantage that the reactor costs will be minimal because of the mild reaction temperature and pressure.

The findings by Nicol, Podrebarac, Huang and others make way for an alternative production process for diacetone alcohol that combines the benefits of mild reaction conditions and heterogeneous catalysis, namely electrosynthesis. Electrosynthesis uses electrons to activate molecules, making it a versatile and inherently environmentally friendly technique and therefore it is being considered as a “clean” and “green” process [28]. Electrosynthesis offers several important advantages to conventional synthetic methods, such as less aggressive process conditions (reactions can be carried out at ambient temperature and pressure), higher selectivity (precise control of reaction by control of electrode potential), ability to produce unstable or hazardous reagents in situ and less generation of pollutants and waste streams [29–31]. Though electrochemical processes often proceed in dilute solutions which require a purification afterwards to increase the concentration of the target product, its properties imply a much less profound and costly purification than the conventional chemical route [28]. Due to the increased selectivity (less byproducts, if any), the absence of a catalyst which has to be removed or regenerated and the readily reusable product stream a single separation step such as a simple distillation (in contrary to a complex rectification), membrane separation or absorption step can be sufficient. The advantages inherent to electrosynthesis make it an interesting and useful alternative: more than 100 processes have been piloted and more than 70 have been commercialised in the industry [29,32].

The electrochemical aldol condensation has been investigated by Shono et al. [33]. They report the self- and cross-condensation of a small number of aldehydes at a platinum electrode in dimethylformamide (DMF) with a quaternary ammonium salt as supporting electrolyte. The reactions proceed at reduction potentials of –1.8 to –2.1 V vs. the saturated calomel electrode (SCE) with yields of about 75%. Shono et al. suggest that the reaction proceeds indirectly through the formation of an electrogenerated base (EGB). Electrogenerated bases are most commonly radical anions, anions or dianions, which after formation initiate another reaction [30,31]. A similar investigation was performed by Kumar et al. [34] who studied the aldol condensations of propanal with itself and with a small number of other aldehydes. They also used a platinum electrode, but the electrolyte consisted of 50% DMF and 50% water with KCl as supporting electrolyte. The reactions take place in a potential range of –1.55 to –2.20 V vs. SCE with yields of 55–80%. Kumar et al. also suggest that the reaction proceeds through the formation of an EGB, but propose a more detailed possible mechanism. The electrochemical aldol condensation of diacetone alcohol was also briefly investigated by Tsai et al. who reported the results in three papers [35–37]. Similar to Shono et al. and Kumar et al. these papers describe a preliminary investigation to the feasibility of the reaction, which confirms the possibility of the electrochemical pathway, but offers no information towards industrial development or implementation. In the first investigation [35], a solution of 4 M acetone in water with 2.5 M KCl was galvanostatically electrolysed, which resulted in millimolar concentrations of diacetone alcohol and cell potentials ranging from 3.2 to 5.2 V. When the acetone concentration was increased to 10 M in the set-up used, the potential further increased to 14 V. The high potentials correspond with a high energy consumption

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