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Catalytic synthesis of butylketene and hexylketene from hexanoic acid and octanoic acid on functionalized silica monoliths at short contact times

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Abstract

Butylketene and hexylketene have been synthesized by catalytic dehydration of hexanoic and octanoic acids, respectively, over functionalized silica monoliths. The efficacy of silica for production of low molecular weight ketenes can be extended to higher molecular weight ketenes without any compromise in selectivity. For instance, the catalytic dehydration of octanoic acid was demonstrated to produce hexylketene with carbon selectivities on the order of 90% at temperatures between 745 and 795 K over a functionalized silica monolith. The results indicate that the control of contact time is a valid strategy for maximizing yield in catalytic ketene synthesis. Also, the ketene synthesis process can be integrated easily with ketene derivatization to prepare esters, in high yields.

Keywords: Ketenes; Butylketene; Hexylketene; Hexanoic acid; Octanoic acid; Silica monolith

1. Introduction

Ketenes with alkyl groups containing 10–20 carbons are produced from natural fatty acids by dehydrohalogenation of their corresponding acid chlorides with stoichiometric quantities of tertiary amines, like Et_3N, in an organic solvent [1]. These aldoketenes are very reactive and dimerize in situ to produce the lactone dimers which have been used as sizing agents for the paper industry. This technology is a non-catalytic, multiple step process involving toxic and corrosive reactants, solvents and by-products which must be disposed adequately. The direct synthesis of higher molecular weight ketenes by catalytic dehydration of carboxylic acids on silica monoliths could represent a more benign and environmentally safer alternative to the dehydrohalogenation technology.

Martinez et al. [2,3] reported that ketene and dimethylketene can be synthesized by dehydration of acetic acid and isobutyric acid, respectively, over functionalized silica monoliths. Molar yields of ketene and dimethylketene of more than 80% per pass were routinely achieved. These results and the fact that the catalytic production of C_2–C_5 ketenes showed no significant dependence on carbon number [4,5] make technically feasible the production of higher molecular weight ketenes by catalytic dehydration of the corresponding carboxylic acid over functionalized silica monoliths.

However, there are some experimental barriers to the catalytic dehydration of higher molecular weight carboxylic acids. The first is the low vapor pressure of fatty carboxylic acids [6]. As the carbon number increases, the vapor pressure of the straight-chain carboxylic acids decays exponentially. Therefore, it is more difficult to introduce the acid into the monolith reactor by the method used for acetic and isobutyric acid experiments: passing the inert carrier gas through a bubbler containing the liquid carboxylic acid [3]. Therefore, hexanoic acid (caproic acid) and octanoic acid (caprylic acid) were chosen because they provide an adequate vapor pressure

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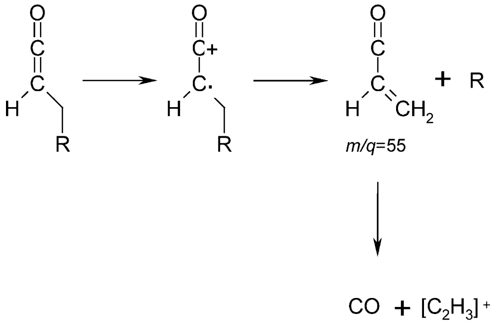
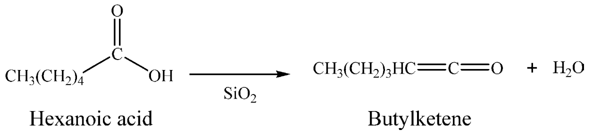
using the same experimental setup as for low molecular weight acids. However, a silicon oil bath was used instead of the water bath to reach higher bubbler temperatures and obtain higher values of the vapor pressure.

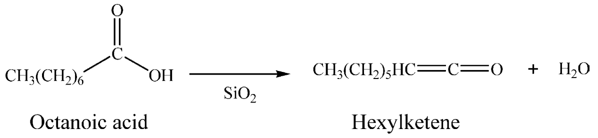
The second experimental problem is to find the adequate analytical technique to quantify the production of higher molecular weight ketenes in real time. The mass spectrometry (MS) has been reported to do so. However, the application of mass spectrometry as an analytical technique for the quantitative determination of the high molecular weight ketenes can be a difficult and challenging task. Of the ketene family, only the cracking patterns for ketene and dimethylketene have been recorded in the standard MS databases [7,8]. Because of the high reactivity of ketenes, few MS studies have been reported where the substrates themselves are introduced directly into the spectrometer [9,10]. Barteau and co-workers used MS for the catalytic dehydration of the carboxylic acids [4,5]. They used the signals for the parent mass of the ketenes and those at *m*/*q* values 1 and 28 mass units less to identify and quantify the C_2–C_5 ketenes. Maquestiau et al. [11] reported an extensive MS study of a series of alkylketenes synthesized by flash vacuum thermolysis of acid chlorides at 773–873 K. Some important conclusions can be drawn from that study. First, the cracking patterns of alkylketenes are very simple while those of carboxylic acids and carboxylic acid derivatives are rather complex. Second, the molecular ion peak for alkylketenes is, in general, very intense and this ion peak is the largest one for the case of ketene, methylketene, and ethylketene. For propylketene, butylketene, and pentylketene, the molecular ion peaks are still intense but the largest fragmentation is $m/q = 55$ for all of them. These results suggest that the main fragmentation pathway for alkylketenes is loss of an alkyl group by β-cleavage followed by loss of CO as depicted in the following scheme [11]:



The authors also reported that when competitive β-cleavages are possible, the preferential elimination of the largest radical is observed. For the case of butylketene, Maquestiau et al. reported that the fragment, $m/q = 55$ is the most abundant, followed by the parental fragment, $m/q = 98$. Other detected fragments were $m/q = 27$, 42, 41, and 28. In our work, all these signals were monitored to track the formation of butylketene by catalytic dehydration of hexanoic acid on functionalized silica monoliths.



Also, the cracking principles observed from C_2–C_7 alkylketenes by Maquestiau et al. may be used to predict the fragmentation pattern for the hexylketene expected as the product of octanoic acid dehydration.



The fragment, $m/q = 55$, will be the principal hexylketene fragmentation channel. The signal for the parent mass at $m/q = 126$ must be present as well as signals from the β-cleavage and the CO loss, $m/q = 71$, 98, and 28. In this investigation, all of these signals were checked as fingerprints to track the formation of hexylketene by catalytic dehydration of octanoic acid on functionalized silica monoliths.

The goals of these experiments are to test the feasibility of the catalytic dehydration of heavier carboxylic acids (hexanoic acid and octanoic acid) to produce the corresponding alkylketenes using functionalized silica monoliths and to determine whether the short contact time approach is useful to promote higher alkylketene selectivity.

2. Experimental

2.1. Functionalized monolith preparation and characterization

The catalyst was prepared using the procedure patented by Martinez et al. [2]. Surface areas of plain and functionalized silica monoliths were measured by the BET method (Micromeritics 2010 ASAP). The samples were baked at 473 K overnight before measurements. While the surface area of the plain monolith was less than 2 m^2/g, the functionalized monolith had an enhanced surface area of 50 m^2/g. The morphology of the amorphous silica deposits was observed by optical microscopy (Nikon SMZ-2T).

2.2. Reactor setup

The reaction system has been described previously [3]. All the carboxylic acids (hexanoic acid 99.5%, Aldrich; octanoic acid 99.5%, Aldrich) were used as received. A hot silicone oil bath with a temperature controller was used to heat up the bubbler. The reactants, bubbler temperatures, and dosing conditions in the mass spectrometer are tabulated in Table 1.

A quadrupole mass spectrometer (MKS, Orion® Compact) with a differentially pumped UTI atmospheric pressure sampling module (APSM) was used to monitor product and