PERP Program

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Chem Systems' Process Evaluation/Research Planning program has published a new report, ***Alkyl Vinyl Ethers (97/98S6)***.

Vinyl ethers are perhaps the least commercially exploited of all vinyl monomers. One of the reasons for this is that the historical synthesis of the vinyl ether group uses difficult to handle acetylene (base catalyzed vinylation of alcohols):

$$ROH + CH\equiv CH \xrightarrow{KOH} RO{-}HC{=}CH_2$$

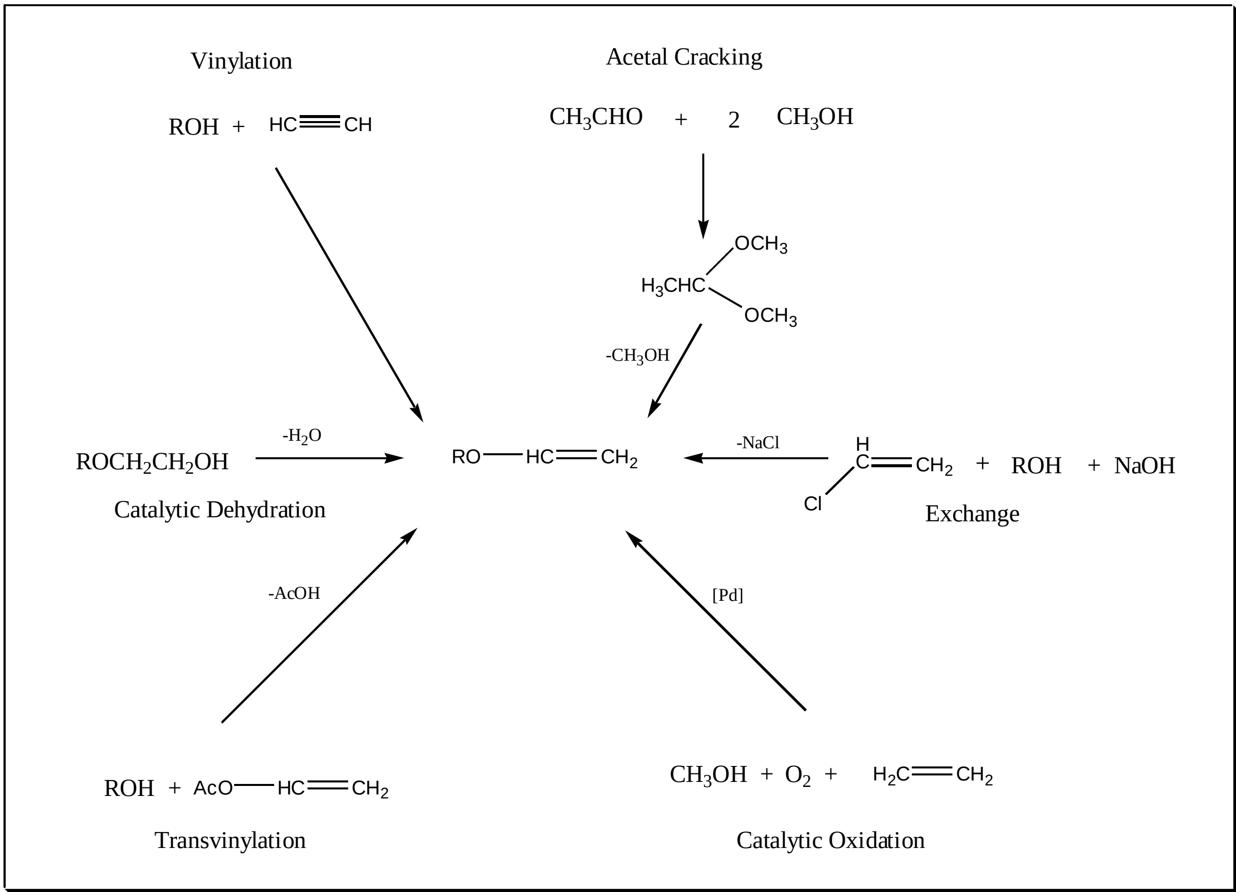
The expertise to handle acetylene safely at the pressures normally needed to achieve commercially acceptable rates was originally developed by Reppe in Germany in the 1930s. BASF became the industrial concern to first commercialize the acetylene based route to vinyl ethers in Europe. This expertise was also transferred to an affiliated company in the United States. This company later became an independent entity known as GAF. The chemical operations of GAF are today known as International Specialty Chemicals (ISP). For many years, BASF and ISP practiced the manufacture of vinyl ethers, whereas those, perhaps inclined to produce vinyl ethers, were precluded because of their inability to handle acetylene safely.

In efforts to circumvent the need to use acetylene, other methods to make vinyl ethers have been explored over the years. The most successful alternative method has been commercialized by Union Carbide and involves the cracking of acetaldehdye dimethyl acetal to afford methyl vinyl ether. Recently, Nippon Shokubai (NSKK) patented a method that employs the catalytic dehydration of glycols or glycol ethers. NSKK has indicated that it has plans to commercialize such a process.

Several other routes have also been looked at, but never commercialized. For example, one method involves mercury or palladium catalyzed transvinylation from vinyl containing materials like vinyl acetate, vinyl pyrrolidone, or vinyl chloride to alcohols. This route suffers from relatively low yields due to equlibrium constraints. Still another route is analogous to the Wacker process for making vinyl acetate from acetic acid and ethylene. In the case of methyl vinyl ether, methanol, ethylene, and oxygen are reacted over a palladium catalyst. The problem with this approach is that, unlike the vinyl acetate case where acetic acid reactant is relatively resistant to further oxidation, methanol can undergo unwanted oxidative side reactions that deleteriously affect yield of the desired methyl vinyl ether. Exchange of the chloride in vinyl chloride monomer with an alkoxy group by reaction with an alcohol is yet another route to vinyl ethers. This method is not favored thermodynamically, and the reaction must be driven by reacting the evolved HCl with a base. The various routes are shown below. This report explores acetylene vinylation, acetal cracking and glycol dehydration routes and compares the production economics of these three methods.

The single largest non-polymer application for vinyl ethers is for methyl vinyl ether (MVE) used in the production of glutaraldehyde. Other lower vinyl ethers such as ethyl-, isobutyl-, and *n*-butyl vinyl ethers are employed as intermediates in the production of a variety of specialty products including pharmaceuticals, flavors, and fragrances.

ROUTES TO VINYL ETHERS



Vinyl ether/maleate copolymers are used primarily in oral care and hair care applications. Their bioadhesive properties give them an advantage as the key ingredient in denture adhesive formulas. They are also used in toothpaste formulations. Vinyl ether/maleate half ester copolymers are used in hair care applications as hair fixatives in aerosol and pump hair sprays, mousses, and setting lotions. These copolymers form tough glossy tack-free films and have excellent hair-holding properties and moisture resistance.