

# Synthesis of Precursors to Ethylene Glycol from Formaldehyde and Methyl Formate

Fuat E. Celik, Henry Lawrence, and Alexis T. Bell\*  
Department of Chemical Engineering  
University of California, Berkeley, CA 94720-1462  
\*bell@cchem.berkeley.edu

## Introduction

Ethylene Glycol (MEG), an important industrial chemical used in the synthesis of polyesters, is currently produced from crude-oil derived ethylene. Producing ethylene glycol from synthesis gas derived methanol and its derivatives, such as formaldehyde and methyl formate, holds economic promise.

Formaldehyde carbonylation using a strong acid catalyst produces glycolic acid (GA) [1-3]. GA can be esterified to methyl glycolate (MG) and then hydrogenated to MEG and methanol. Reaction mixtures of water and formaldehyde in an autoclave containing a strong acid catalyst (e.g., an acid resin, mineral acid, or heteropoly acid) and pressurized with CO to 240 bar can yield ~ 80% MG after esterification [3].

The very high pressures required because of low CO solubility are undesirable, and so an alternative to high-pressure carbonylation of formaldehyde is preferable. Recent efforts to develop carbonylation chemistry without the direct use of carbon monoxide have looked at formic acid and methyl formate (MF) as CO carrier molecules [4]. MF will decompose to give CO in solution plus methanol. Carbonylation of formaldehyde with MF using heteropoly acid catalysts has been shown to give MG and methyl methoxyacetate (MMAc) [5]. MMAc can also be converted to MEG via hydrolysis and hydrogenation, or directly hydrogenated to glycol ether, an important industrial solvent.

## Materials and Methods

In the present study, MG and MMAc were synthesized from formaldehyde and MF in a 25 ml Parr Instruments autoclave. Silicotungstic acid,  $H_4SiW_{12}O_{40}$  ( $SiW_{12}$ ) was used as the catalyst. Formaldehyde was introduced as oligomeric paraformaldehyde. Formaldehyde (2 g), methyl formate (4 g), catalyst (0.25 g) and methanol (0.5 g) were mixed and heated to 150°C for 3 h. Methanol was added to prevent repolymerization of formaldehyde as polyoxymethylene. In most reactions, no external CO pressure was applied. Liquid phase products were analyzed quantitatively by gas chromatography. The effect of reaction variables such as temperature, duration, methanol concentration, formaldehyde source, and catalyst composition were studied.  $SiW_{12}$  was purchased (Aldrich) and calcined at 300°C in He for 3 h prior to use.

## Results and Discussion

In the presence of excess methanol, dimethoxy methane (DMM) is the primary product of the reaction. Reducing methanol concentration favors the carbonylation products MG and MMAc. During reaction, up to 30 atm of CO were generated from MF. CO pressure

accumulated in the reactor linearly with time, and concentrations of MG and MMAc were low for short reaction times. Substituting equivalent amounts of MF with CO and methanol showed that increasing CO availability in the reactor boosted MG and MMAc production. Pressurizing the reactor with gaseous CO in addition to the original amount of MF showed even higher yields of MG and MMAc. This suggests that release of CO from MF is a limiting step in the reaction. In contrast, DMM formation occurs quickly, even at low temperature, and DMM acts as a reversible source of formaldehyde throughout the reaction.

Solutions produced under reaction conditions were colored light yellow to dark brown. The color arises due to the formation of formose sugars from formaldehyde and their subsequent carbonization by the acid catalyst [2] in an undesired side reaction. The mechanism for sugar formation under acidic conditions is unknown.

Reactions between DMM and MF showed that DMM could be carbonylated to MG and MMAc under the same conditions as formaldehyde, and that yields were slightly higher.

The activity of  $SiW_{12}$  was compared to other heteropoly acids. Phosphotungstic acid,  $H_3PW_{12}O_{40}$  ( $PW_{12}$ ) showed lower activity, both on a per mass and per proton basis, despite its slightly stronger acidity. Both silicomolybdic and phosphomolybdic acid were much less active. The lower activity of molybdic acids corresponds to their greater reducibility, as reduced heteropoly acids are weaker acids than fully oxidized ones. The greater activity of  $SiW_{12}$  over  $PW_{12}$  is attributed to the softness of the heteropoly anion formed after transfer of a proton to formaldehyde. The soft anion helps stabilize the carbocation intermediates before and after CO addition, and thereby promotes the overall reaction.

A reaction scheme was developed relating the observable products to the proposed intermediates and starting materials. Protonation of formaldehyde produces the carbocation  $(HO)H_2C^+$ , which can be carbonylated to give MG. Reaction with methanol gives methoxymethanol,  $CH_3OCH_2OH$ , which is protonated to give a second carbocation,  $(CH_3O)H_2C^+$ . Reaction with CO gives MMAc, and reaction with methanol gives DMM.

## Significance

In this study, high pressure carbonylation was avoided by using MF as the CO source. DMM was shown to be an effective formaldehyde source for the synthesis of MG and MMAc. Slow release of CO from MF was identified as the major limiting factor in using MF to carbonylate formaldehyde, and the relative activity of different heteropoly acid catalysts was tested and rationalized. Finally, a scheme was developed relating products to reactants and intermediates.

## References

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