Synthesis of precursors to ethylene glycol from formaldehyde and methyl formate catalyzed by heteropoly acids

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ABSTRACT

The production of ethylene glycol from methanol and its derivatives, such as formaldehyde, is potentially attractive, since the carbon needed for such a process can be derived from synthesis gas, a cheaper carbon source than petroleum-derived ethylene. This study reports an investigation of formaldehyde carbonylation using methyl formate as the source of CO. Silicotungstic acid and other heteropoly acids were used as the catalyst. Methyl glycolate and methyl methoxyacetate, both precursors to ethylene glycol, were formed along with dimethoxymethane and dimethyl ether, the primary byproducts. The effects of formaldehyde source, reaction temperature, time, and catalyst were investigated. Methoxymethanol, paraformaldehyde, 1,3,5-trioxane, and dimethoxymethane were examined as sources of formaldehyde. The highest yields of methyl glycolate and methyl methoxyacetate were obtained using 1,3,5-trioxane as the source of formaldehyde. Release of carbon monoxide from methyl formate was found to be slow and limited the rate of carbonylation. Of the heteropoly acids investigated, silicotungstic acid produced the highest yields of methyl glycolate and methyl methoxyacetate, whereas methanesulfonic acid did not produce these products at similar acid loading. The difference in the effectiveness of heteropoly acids and methanesulfonic acid is ascribed to the role of the anion of the heteropoly acid, a soft base, in stabilizing the reactive intermediates involved in the carbonylation of formaldehyde.
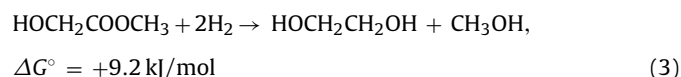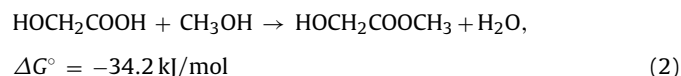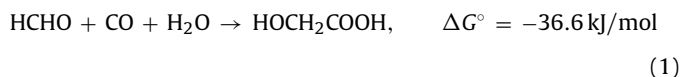
1. Introduction

Ethylene glycol (monoethylene glycol—MEG) is an important industrial chemical used in the manufacture of polyester resins and fibers and antifreeze. While global antifreeze demand is stable, demand for polyester is increasing at roughly 10% per year, driven mainly by growth in China [1]. Demand for ethylene, the raw material used to make MEG, is outpacing supply, leading to price increases for MEG [2]. Replacing ethylene derived ultimately from crude oil, with syngas derived from natural gas, coal, or biomass could be economically competitive and increase MEG supply for the growing polyester market.

Direct synthesis of MEG from syngas is possible but requires pressures of 1300–7000 atm, temperatures above 200 °C, and gives very low yields [3,4]. MEG synthesis starting from methanol, formaldehyde, or other C_1 compounds that can be produced from syngas are referred to as indirect routes. Some examples include hydroformylation of formaldehyde [5,6], oxidative coupling of CO in methanol [7], and carbonylation of formaldehyde [8,9]. Of these, formaldehyde carbonylation has been practiced commercially by DuPont [8,10,11].

The acid-catalyzed carbonylation of formaldehyde occurs by the Koch mechanism, beginning with the protonation of the substrate to yield a carbocation, which undergoes CO addition to give a resonance-stabilized acyl carbocation in the carbon-carbon bond-forming step. Water addition and subsequent deprotonation yields glycolic acid (GA). Glycolic acid, as an intermediate to MEG, is esterified with methanol to methyl glycolate (MG), and then hydrogenated in the final step to yield MEG. The stoichiometric reactions involved in this process are shown below:

$$HCHO + CO + H_2O \rightarrow HOCH_2COOH, \qquad \Delta G^\circ = -36.6\,kJ/mol \tag{1}$$

$$HOCH_2COOH + CH_3OH \rightarrow HOCH_2COOCH_3 + H_2O,$$
$$\Delta G^\circ = -34.2\,kJ/mol \tag{2}$$

$$HOCH_2COOCH_3 + 2H_2 \rightarrow HOCH_2CH_2OH + CH_3OH,$$
$$\Delta G^\circ = +9.2\,kJ/mol \tag{3}$$

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The DuPont process for MEG synthesis via formaldehyde carbonylation achieved yields in excess of 96% using H_2SO_4 as the catalyst [10,11]. The reaction required 900 atm of CO pressure and temperatures between 150 and 200 °C. All reactants in the DuPont process were prepared from coal-derived syngas. Corrosive reaction conditions associated with using a mineral acid and high pressures of CO led to discontinuation of the technology in 1968 [8].

Renewed interest in formaldehyde carbonylation arose with the use of solid acids replacing sulfuric acid. Solid acids have a number of benefits over mineral acids, including ease of catalyst recovery, stronger acidity, and less corrosion. Hendriksen [9] has reported 48% yield of GA with CO pressure as low as 102 atm (1500 psi) using Nafion perfluorosulfonic acid resin at 150 °C, and 79% yield at 313 atm (4600 psi). Lee et al. [8] have investigated a number of acidic resins as well as two heteropoly acids (HPAs), $H_3PW_{12}O_{40}$ (PW_{12}), and $H_3PMo_{12}O_{40}$ (PMo_{12}). They achieved 36% yield of MG after esterification with 68 atm (1000 psi) of CO and 81% yield with 238 atm (3500 psi) using Amberlyst, a polystyrenesulfonic acid resin.

The high-pressure requirement of formaldehyde carbonylation is due to low solubility of CO in the liquid phase. In the original DuPont process water was the only solvent, and at 150 °C and 60 atm of external CO pressure, the solubility of CO in water is only 0.054 mol/l [12]. Increasing the pressure to 900 atm increases the solubility to 0.81 mol/l. Hendriksen and Lee et al. used 1,4-dioxane as their solvent, for which the solubility is 0.56 mol/l at 150 °C and 60 atm CO pressure [13]. Much of the apparent decrease in required pressure can be attributed to the change in solvent. Despite the reduction, the pressure requirement is still considerable.

There has been recent interest in developing carbonylation chemistry without the use of gaseous CO [14]. Methyl formate (MF) has been suggested as a viable means for providing CO [15], since it can be decarbonylated catalytically to CO and methanol:

$$HCOOCH_3 \rightarrow CO + CH_3OH, \qquad \Delta G° = +0.4 \text{ kJ/mol} \qquad (4)$$

Similarly, formic acid (FA) can be used to give CO and H_2O. Hendriksen [9] mentions that if MF is used, no additional CO pressure is required for the carbonylation of formaldehyde. In this reaction, MF acts as the sole CO source, and MG is produced directly instead of GA:

$$HCOOCH_3 + HCHO \rightarrow HOCH_2COOCH_3, \qquad \Delta G° = -70.4 \text{ kJ/mol} \qquad (5)$$
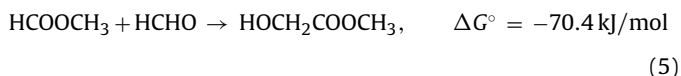
The release of methanol from reaction (4) leads to methyl methoxyacetate (MMAc):

$$HCOOCH_3 + HCHO + CH_3OH \rightarrow CH_3OCH_2COOCH_3 + H_2O,$$

$$\Delta G° = -96.4 \text{ kJ/mol} \qquad (6)$$
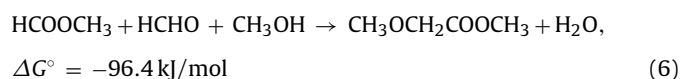
MMAc can be hydrolyzed and then hydrogenated to give MEG, or hydrogenated directly to glycol ether, an important industrial solvent.

He et al. [16,17] have compared the activity of a number of mineral, organic, and solid acids, including PW_{12}, PMo_{12}, $H_4SiW_{12}O_{40}$ (SiW_{12}), and $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$) for the carbonylation of formaldehyde with methyl formate. In their work, SiW_{12} and PW_{12} gave the best yields of MG and MMAc. Further study [18,19] showed that salts of SiW_{12} were less active than the parent acid, and that water was detrimental to product yield. A similar reaction between formaldehyde and formic acid in water to produce GA has also been shown using HCl as the catalyst [20].

The aim of the work presented here was to establish the effects of formaldehyde source, reaction temperature, and reaction time on the acid-catalyzed carbonylation of formaldehyde with methyl formate. Following the work of He et al. [18], HPAs were chosen as catalysts for this study, with particular interest in SiW_{12}. A reaction scheme describing the important chemistry was developed and used to explain the effects of reaction conditions on the distribution of observed products. The role of catalyst composition was also explored. This part of the investigation revealed the importance of the HPA anion composition in dictating the activity and selectivity of HPAs. In this paper, MG and MMAc are referred to as C_2 compounds as they contain only one carbon–carbon bond.

2. Experimental methods

All reactions were carried out in a 25 ml Hastelloy C-276 autoclave (Parr Instruments), equipped with a temperature-programmed electric heating mantle, a magnetically driven Teflon coated stir bar, a Hastelloy C-276 thermowell containing an iron–constantan J-type thermocouple, and a gas pressure gauge. Hastelloy C-276 was chosen as the material of construction because of its broad corrosion resistance.

Paraformaldehyde (Aldrich) and 1,3,5-trioxane (Aldrich) were used as the sources of formaldehyde. In addition, formaldehyde methyl hemiacetal (hereafter referred to as methoxymethanol) was prepared by heating paraformaldehyde to 100 °C and bubbling the vapors through methanol at room temperature. A flow of 100 ml/min He was used to carry the vapors and the transfer tube was heated above 150 °C to prevent repolymerization of formaldehyde. A 39 wt% formaldehyde solution was prepared this way. Formaldehyde dimethyl acetal (hereafter dimethoxymethane, DMM), obtained from Sigma–Aldrich was also used as a formaldehyde source in some experiments. Reagents were used without further purification.

Heteropoly acids SiW_{12}, PW_{12}, $SiMo_{12}$, and PMo_{12} were obtained from Sigma–Aldrich and Strem Chemicals. Prior to use, these materials were dehydrated in a 50 cm^3/min He flow for 3 h at 300 °C according to He et al. [18].

In a typical reaction, the autoclave was loaded with 2 g of paraformaldehyde, 4 g of methyl formate, and 0.25 g of an acid catalyst. Methanol (0.5 g) was added to stabilize formaldehyde. The autoclave was then sealed. Additional gases could be added to the reactor through a gas inlet valve. The contents of the reactor were stirred and heated to 150 °C. The reaction temperature was reached after approximately 25 min. After 3 h at 150 °C, the reactor was cooled in an ice bath for approximately 30 min.

Liquid-phase products were analyzed by gas chromatography using an Agilent 6890n GC. MF, DMM, MG, and MMAc concentrations were quantified using an HP-PLOT Q bonded polystyrene-divinylbenzene capillary column and a flame ionization detector. H_2O, HCHO, and CH_3OH concentrations were determined using a HayeSep DB divinylbenzene packed column and a thermal conductivity detector. A known mass (3.5–3.9 mg) of cyclohexane was added to a known mass of reaction liquid ($\sim$1 g) as an internal standard. Gas-phase CO was analyzed with a HayeSep DB column and GC TCD.

3. Results and discussion

3.1. Reactions with methoxymethanol as formaldehyde source

Initial experiments were carried out using methoxymethanol, the methyl hemiacetal of formaldehyde, as a monomeric formaldehyde source. The methoxymethanol solution prepared contained 39 wt% equivalent formaldehyde, 1 wt% water, and balance methanol. Typically, 3 g of 39 wt% HCHO solution and 3 g of MF
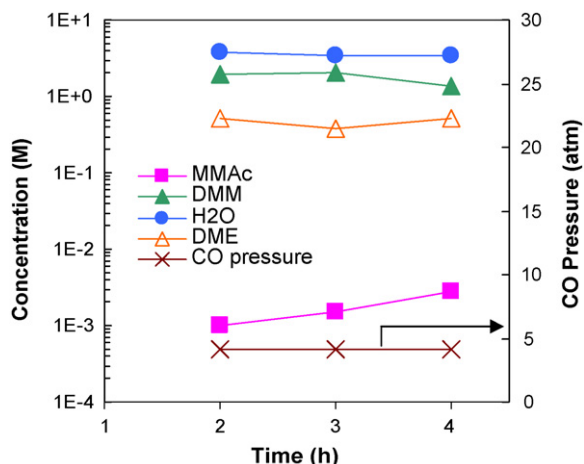
Fig. 1. Effect of reaction time on product distribution using methoxymethanol as the formaldehyde source. $T = 150\,°C$. $SiW_{12} = 0.088$ mmol, HCHO = 39 mmol as methoxymethanol solution, $CH_3OH = 48$ mmol, MF = 50 mmol.

were used. Reaction temperature and duration were varied, with results shown in Figs. 1 and 2.

During reaction, CO released by MF decomposition (reaction (4)) accumulated in the reactor head space. CO release increased with temperature from 135 to 165 °C, as did the concentrations of MG and MMAc. The solutions produced in these reactions were colored, ranging from pale yellow to very dark brown/black, with darker solutions produced at higher temperatures. In some reactions, a black solid was collected from the bottom of the reactor. Hendriksen [9] has reported a similar observation for a slightly different reaction system, and attributed the color to the formation of formose sugars from formaldehyde, which subsequently underwent acid-catalyzed carbonization. Formose chemistry is well known in the presence of bases [21], but is not possible under acidic conditions. Thus, we propose that the color may be due to the formation of polymers of glycolic acid or the acid-catalyzed carbonization of other reaction components (see for example reaction (7)). Polymers of glycolic acid copolymerized with formaldehyde give rise to yellow liquids, and those without formaldehyde are brown solids [22]:
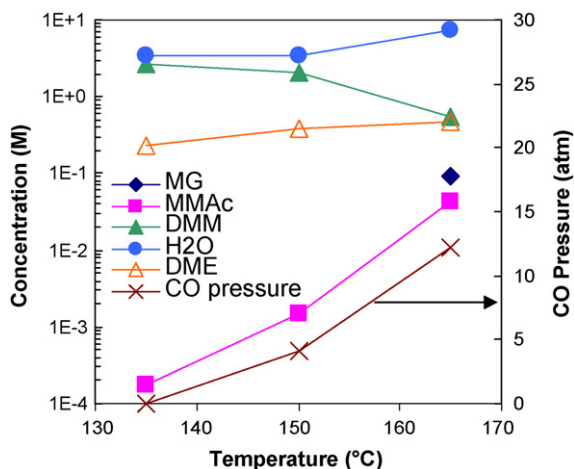
$$nHCHO \rightarrow C_{n(s)} + nH_2O \qquad (7)$$

Fig. 2. Effect of reaction temperature on product distribution using methoxymethanol as the formaldehyde source. Time = 3 h. $SiW_{12} = 0.088$ mmol, HCHO = 39 mmol as methoxymethanol solution, $CH_3OH = 48$ mmol, MF = 50 mmol.
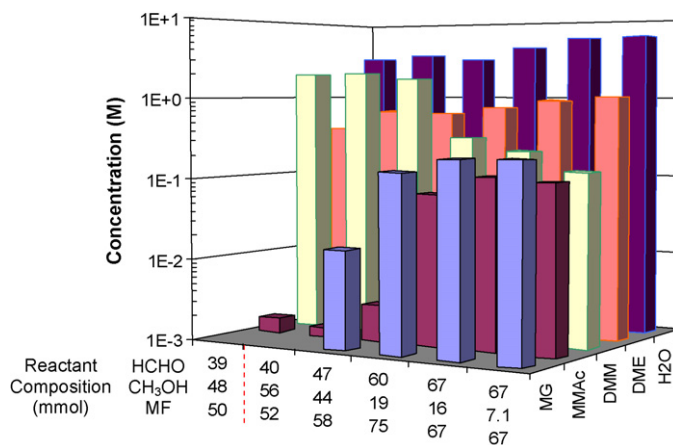

Fig. 3. Effect of methanol content on product distribution using methoxymethanol and paraformaldehyde as the formaldehyde source. Time = 3 h, $T = 150\,°C$, $SiW_{12} = 0.088$ mmol. The first data set uses a 39 wt% HCHO solution in CH_3OH as the HCHO source. All others use paraformaldehyde.

Because of the large excess of methanol, DMM was formed as the primary product, by reaction (8). DMM concentration was stable between 2 and 4 h. MMAc was produced at only low concentration, and MG was not observed below 165 °C, even after 4 h:

$$CH_3OCH_2OH + CH_3OH \rightarrow CH_3OCH_2OCH_3 + H_2O,$$
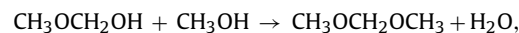
$$\Delta G° = -16.9\,kJ/mol \qquad (8)$$

Reaction (8) produces equal amounts of DMM and water, and at 150 °C, between 2 and 4 h, the concentrations of DMM and water were almost equal. At 135 °C, the concentrations of these products are even closer to each other. With increasing temperature, the concentrations of DMM and H_2O began to diverge, the DMM concentration decreasing and the water concentration increasing. Additional water production came from the dehydration of methanol to form dimethyl ether (DME). Water release from reaction (6) was insignificant as the MMAc concentration was low. The remaining source of water is believed to be the carbonization of reactants and/or products as in reaction (7). The reduction in DMM concentration at higher temperature coincided with an increase in MMAc concentration and the formation of MG as a reaction product.

3.2. Reactions with paraformaldehyde as formaldehyde source

To reduce the amount of methanol used, paraformaldehyde/methanol mixtures were substituted for methoxymethanol solutions. The first data set shown in Fig. 3 was obtained using a methoxymethanol solution as the formaldehyde source. The second set, with the same molar composition, was obtained using paraformaldehyde and methanol, reproducing the results from the methoxymethanol experiments. Analysis of the reaction products showed that methoxymethanol had been formed in situ from the addition of methanol to the formaldehyde monomer released from paraformaldehyde. It is assumed that the rate of paraformaldehyde depolymerization was rapid enough so as not to influence the results.

Reduction of the methanol content in the starting mixtures from 38 to 5 mol% (Fig. 3), favored the formation of C_2 products, MG and MMAc, and reduced the concentration of DMM formed. This suggests that formaldehyde participates in two competitive reaction paths, one leading to DMM and the other leading to C_2 products.

For the reactant composition given as the last data set in Fig. 3, corresponding to 5 mol% methanol, some repolymerization of formaldehyde to polyoxymethylene occurred in reactor cold
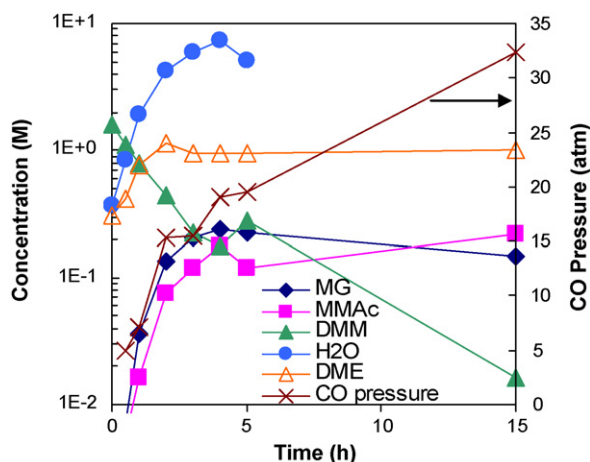
Fig. 4. Effect of reaction time on product distribution using paraformaldehyde as the formaldehyde source. $T = 150\,°C$, $SiW_{12} = 0.088$ mmol, HCHO = 67 mmol as paraformaldehyde, $CH_3OH = 16$ mmol, MF = 67 mmol. Reaction time of 0 h indicates heating to reaction temperature followed by immediate cooling. All other reaction times indicate hold period at reaction temperature.

Fig. 5. Effect of reaction temperature on product distribution using paraformaldehyde as the formaldehyde source. Time = 3 h, $SiW_{12} = 0.088$ mmol, HCHO = 67 mmol as paraformaldehyde, $CH_3OH = 16$ mmol, MF = 67 mmol.

spots, especially in the reactor head assembly. As noted in Section 3.1, methanol stabilizes formaldehyde as the hemiacetal; therefore when the methanol concentration was reduced too far, repolymerization occurred. Maintaining 10 mol% methanol in the starting mixture was sufficient to prevent repolymerization when working with paraformaldehyde in all cases.

When excess methanol was used with paraformaldehyde, the concentrations of water and DMM were nearly equal to each other, as was the case when methoxymethanol was used as the formaldehyde source. Thus, the primary source of the water for these conditions was reaction (8). As the methanol loading was reduced, the DMM concentration decreased but the water concentration increased, indicating a shift from reaction (8) to carbonization reactions, such as reaction (7), as the source of water, with an increasing contribution also coming from reaction (6). DME concentration remained nearly constant, despite the reduction in the initial concentration of methanol in the reactant mixture. This was due to the production of methanol from MF, as evidenced by the increasing CO pressure developed in the reactor. The color of the reaction solutions darkened as the methanol concentration was decreased, further indicating an increase in polymer formation and/or carbonization of reaction components.

The effects of varying reaction time and temperature are given in Figs. 4 and 5. DMM formation occurred at lower temperatures and shorter times than C_2 product formation. In particular, the maximum DMM concentration was obtained when the reactor was heated to $150\,°C$ and then immediately cooled down (a hold time of 0 h) indicating that DMM formation from paraformaldehyde is not only fast, but reaches equilibrium. If DMM had not equilibrated, an increase in hold time to 0.5 or 1 h would be expected to increase the concentration of DMM.

As seen in Fig. 4, CO pressure increased with time. The slow accumulation of gaseous CO in the reactor was due to the apparently slow decomposition of MF. Assuming equilibration between gaseous and dissolve CO, a small CO pressure indicated a low concentration of dissolved CO, and therefore a slower carbonylation rate. Thus, the C_2 product concentrations were small while CO pressure was low for times less than 2 h, and increased with increasing CO pressure up to 5 h. Beyond 5 h of reaction, the concentration of C_2 products did not change significantly despite an increase in CO pressure, possibly due to the consumption of formaldehyde – as evidenced by the disappearance of DMM – to form other byproducts.
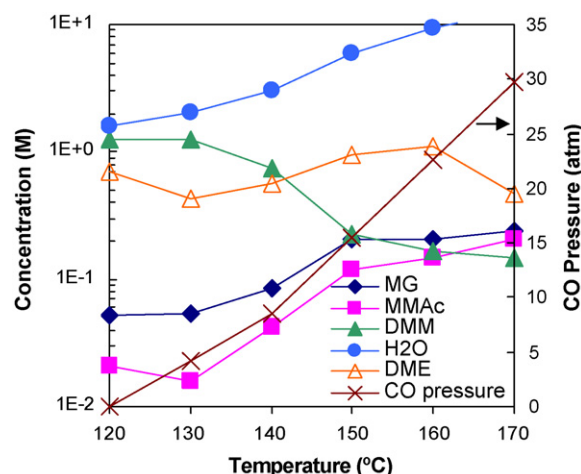
Increasing the reaction temperature increased the concentrations of MG and MMAc (Fig. 5). However, the color of the solutions darkened, indicating an increase in polymer or carbon formation, or both. Water concentration also increased with temperature, consistent with an increased level of carbonization. The increase in C_2 product concentrations at higher temperature is attributed to the higher CO pressure released from MF under these conditions.

To simulate a faster release of CO from MF, some of the initial MF was replaced by methanol and gas-phase CO. 7.0 and 13 mmol of MF were replaced by 7.0 and 13 mmol of CO and CH_3OH in separate experiments. The effect is equivalent to converting 10 and 20% of the MF (as per reaction (4)) prior to loading the reactor, increasing the CO initially available in the reactor. The results, shown in Fig. 6, reveal an increase in C_2 product concentration when CO is available at short times.

In a separate experiment, 11 mmol of CO were added to the gas phase of the reactor without changing the starting amounts of MF or CH_3OH. The added CO increased the C_2 concentration, even more than that achieved by replacing MF with $CO + CH_3OH$. Considering the total amount of CO as being that contained in

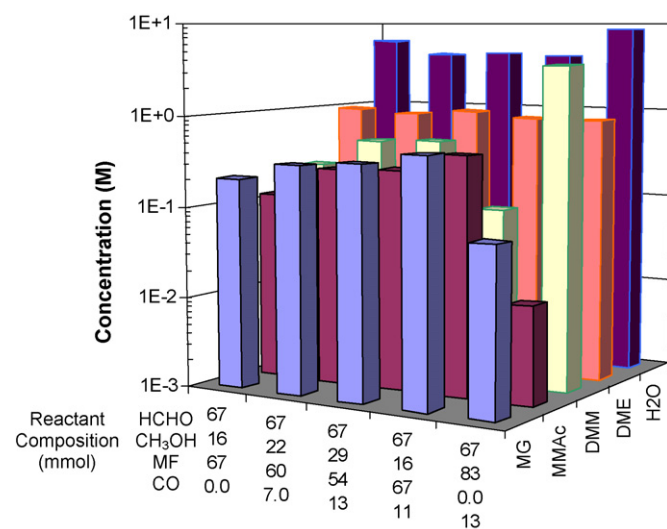**Fig. 6.** Effect of CO content on product distribution using paraformaldehyde as the formaldehyde source. Time = 3 h, $T = 150\,°C$, $SiW_{12} = 0.088$ mmol.

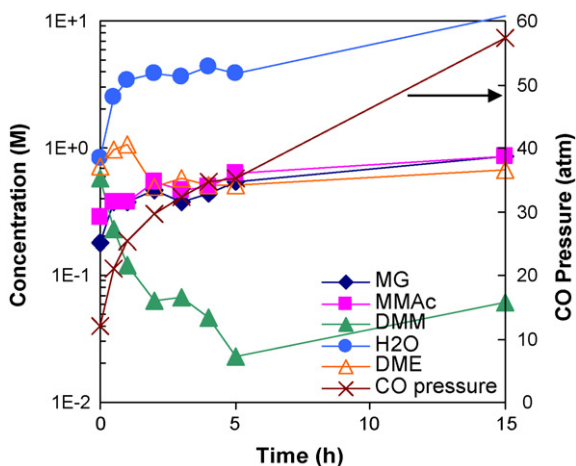**Fig. 7.** Effect of reaction time on product distribution using 1,3,5-trioxane as the formaldehyde source. $T = 150\,°C$, $SiW_{12} = 0.088$ mmol, HCHO = 67 mmol as 1,3,5-trioxane, MF = 67 mmol. Reaction time of 0 h indicates heating to reaction temperature followed by immediate cooling. All other reaction times indicate hold period at reaction temperature.

MF and gaseous CO, this experiment demonstrated that increasing the starting quantity of CO by only 16% led to a 170% increase in C_2 concentration and a 60% decrease in DMM concentration, further suggesting that CO release from MF is a limiting factor in the reaction. The addition of gas-phase CO benefited the formation of MMAc, which increased by 240%, more than it did the formation of MG, which increased by only 130%.

A further experiment attempted the reaction without methyl formate, adding only 13 mmol of CO as a gas to 67 mmol of formaldehyde and 83 mmol of methanol (replacing MF with methanol). Only small amounts of MG and MMAc were observed (Fig. 6), as DMM was by far the majority product due to the large amount of methanol present. This experiment demonstrated that by using MF to release CO slowly, the release of methanol is also slow, thereby inhibiting DMM formation. Although no MF was added to the reaction, a final MF concentration of 1.3 M was observed, indicative of the Cannizzaro coupling of formaldehyde with itself. The MF formed in this way also decomposed to release a net 2.0 atm of CO gas above the CO initially charged to the reactor.

High-water concentrations at the end of some reactions starting with paraformaldehyde led to conversion of a small fraction of the esters in the reaction mixture to their carboxylic acid forms. Formic acid (from MF), glycolic acid (from MG), and methoxyacetic acid (from MMAc) were all detected by GC/MS. Trace quantities of glycol ethers, such as 2-methoxyethanol, 1,2-dimethoxyethane, and 1,3-dioxolane, were also detected by GC/MS.

3.3. 1,3,5-Trioxane as formaldehyde source

When 1,3,5-trioxane was used as the formaldehyde source, no repolymerization of formaldehyde to polyoxymethylene was observed, and so experiments were carried out without adding methanol. Unlike paraformaldehyde, 1,3,5-trioxane is anhydrous, so that no water was introduced at the beginning of the reaction as well. By excluding methanol (except that released from MF) DMM concentrations were lower and C_2 concentrations were higher (Figs. 7 and 8) than those observed when paraformaldehyde was used as the formaldehyde source (Figs. 4 and 5). CO release from MF was also greater, possibly due to the lack of solvent leveling of the acidity for short reaction times. The CO pressure released was nearly double that observed when paraformaldehyde was used as the formaldehyde source (compare Figs. 7 and 4).
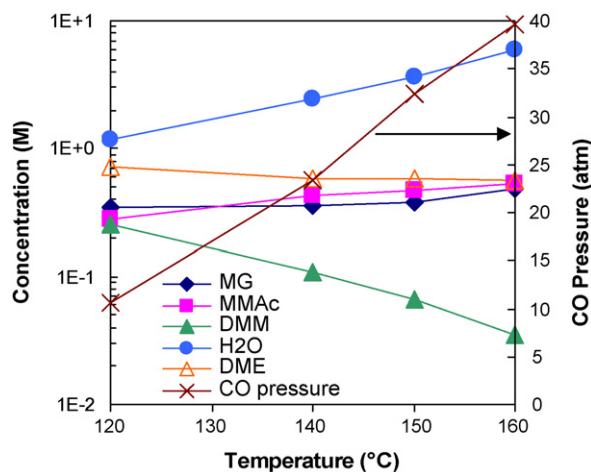

Fig. 8. Effect of reaction temperature on product distribution using paraformaldehyde as the formaldehyde source. Time = 3 h, $SiW_{12} = 0.088$ mmol, HCHO = 67 mmol as 1,3,5-trioxane, MF = 67 mmol.

Unlike paraformaldehyde, which favored MG over MMAc, 1,3,5-trioxane gave nearly equal concentrations of both C_2 compounds. Less water was produced and solutions were generally lighter in color and less solid was collected when 1,3,5-trioxane was used as compared to when paraformaldehyde was used as the formaldehyde source.

3.4. Dimethoxymethane as formaldehyde source

The possibility of DMM carbonylation was explored using both MF and gaseous CO as the source of CO (Fig. 9). In the absence of water, DMM should form only a single product, MMAc (reaction (9)). To form MG, either the ether group of MMAc must be hydrolyzed, or methoxymethanol must be formed as an intermediate. Some water was always produced from the dehydration of methanol released from MF to form DME and from the carbonization reaction. This would explain why MG was always observed
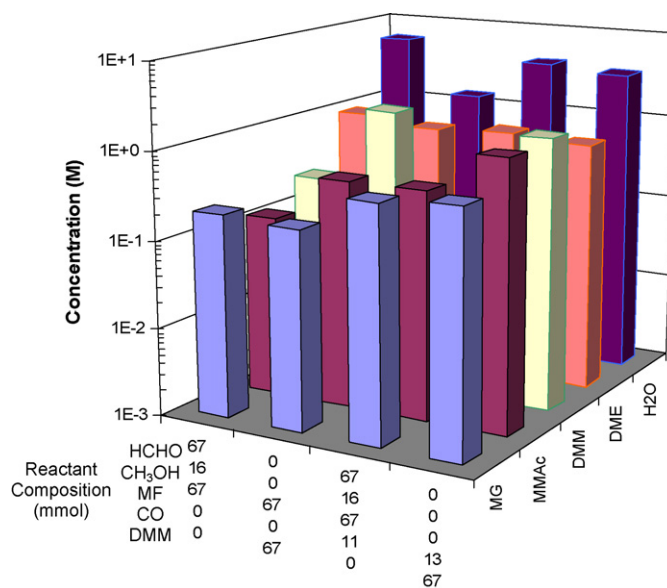

Fig. 9. Effect of CO content on product distribution using paraformaldehyde and DMM as the formaldehyde source. Time = 3 h, $T = 150\,°C$, SiW12 = 0.088 mmol. Comparison of paraformaldehyde and DMM as formaldehyde sources for carbonylation by either MF or CO.

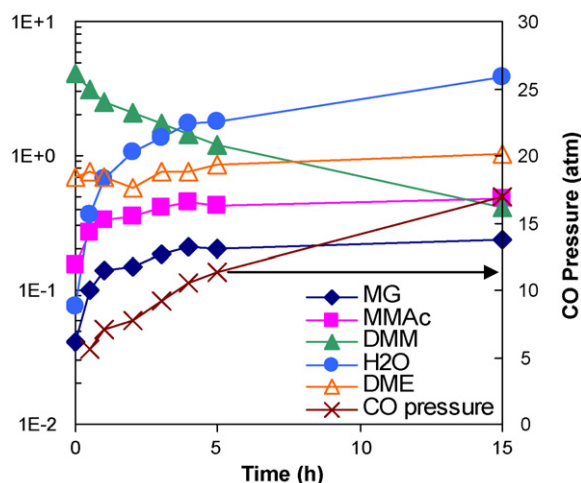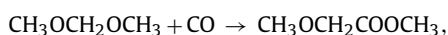**Fig. 10.** Effect of reaction time on product distribution using DMM as the formaldehyde source. $T = 150\,°C$, $SiW_{12} = 0.088$ mmol, HCHO = 67 mmol as DMM, MF = 67 mmol. Reaction time of 0 h indicates heating to reaction temperature followed by immediate cooling. All other reaction times indicate hold period at reaction temperature.

Fig. 11. Effect of reaction temperature on product distribution using DMM as the formaldehyde source. Time = 3 h, $SiW_{12} = 0.088$ mmol, HCHO = 67 mmol as DMM, MF = 67 mmol.

in the reaction products formed. Formation of C_2 products from DMM indicates that the carbonylation of DMM also occurs under conditions where DMM is produced via the reaction of formaldehyde (released from paraformaldehyde or 1,3,5-trioxane) with methanol.

Reactions starting with DMM showed a greater selectivity to MMAc than MG, the reverse of what was observed starting with paraformaldehyde. A comparison of the first and second data sets in Fig. 7 shows that the MG concentration fell by 10% upon switching from paraformaldehyde to DMM, while the MMAc concentration increased by 240%. While the reaction starting with paraformaldehyde generated 13.6 atm of CO, starting with DMM only 9.8 atm of CO were generated:

$$CH_3OCH_2OCH_3 + CO \rightarrow CH_3OCH_2COOCH_3,$$

$$\Delta G° = -68.9\,kJ/mol \tag{9}$$

An experiment starting with only DMM and CO had an even more dramatic result (fourth data set in Fig. 9). The MG concentration was 0.57 M and the MMAc concentration was 1.19 M, the highest of any experiment, accomplished with only 13 mmol of CO, as compared to 67 mmol of MF in most reactions, and 67 mmol of MF plus 13 mmol of CO in the third data set in Fig. 9. The high concentration of C_2 products given the small amount of CO gas present
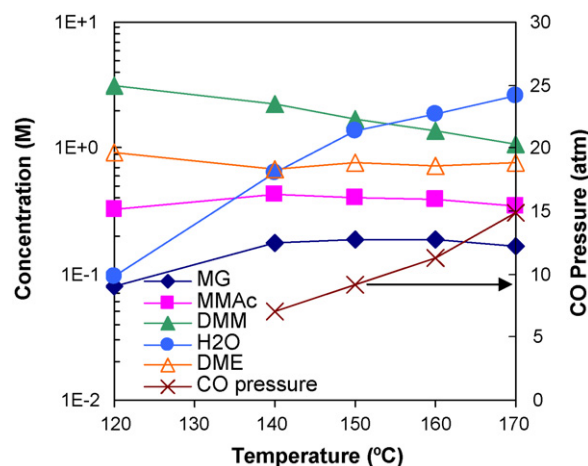
indicates a faster carbonylation rate with DMM than with either paraformaldehyde or 1,3,5-trioxane.

Across a range of reaction times and temperatures (Figs. 10 and 11), reaction solutions were clear and almost colorless, especially when compared to paraformaldehyde, though an appreciable amount of black solid formed in the reactor. Total C_2 product concentration was intermediate between paraformaldehyde and 1,3,5-trioxane (compare Fig. 10 with Figs. 4 and 7). Starting with DMM, MG concentrations were comparable to the lower MG concentrations produced from using paraformaldehyde, and MMAc concentrations were almost as high as the higher MMAc concentrations produced from using 1,3,5-trioxane. The CO pressure generated was nearly one-half of that produced when using paraformaldehyde as the formaldehyde source, and one quarter that produced when 1,3,5-trioxane was used. DMM was also observed to undergo Cannizzaro self-disproportionation as evidenced by the formation of MF as a reaction product when only DMM and CO were loaded into the reactor. The MF generated in this way decomposed to produce additional gaseous CO according to reaction (4).

3.5. Summary of formaldehyde sources

Table 1 summarizes the effects of formaldehyde source on the conversion of formaldehyde to MG, MMAc, DMM, and carbon (measured as H_2O) for a fixed set of reaction conditions. (Water

Table 1
Conversion of formaldehyde and CO to products

Formaldehyde source	$X_{MG,HCHO}$[a] (%)	$X_{MMAc,HCHO}$[a] (%)	$X_{DMM,HCHO}$[a] (%)	$X_{C_{(s)},HCHO}$[b] (%)	$X_{C_2,CO}$[c] (%)
Methoxymethanol[d]	0.0	0.01	15	7.2	0.2
Paraformaldehyde[e]	0.94	0.55	1.0	13	6.5
1,3,5-Trioxane[f]	3.1	3.4	0.28	14	15
DMM[g]	1.5	3.3	5.3[h]	12[i]	41

Time = 3 h, $T = 150\,°C$, $SiW_{12} = 0.088$ mmol.

[a] Conversion of formaldehyde to products as a molar percentage of starting formaldehyde.
[b] Conversion of formaldehyde to $C_{(s)}$ (measured as water less MMAc, DMM, and DME).
[c] C_2 products as a molar percentage of CO generated from MF.
[d] HCHO = 39 mmol as methoxymethanol solution, $CH_3OH = 48$ mmol, MF = 50 mmol.
[e] HCHO = 67 mmol as paraformaldehyde, $CH_3OH = 16$ mmol, MF = 67 mmol.
[f] HCHO = 67 mmol as 1,3,5-trioxane, MF = 67 mmol.
[g] HCHO = 67 mmol as DMM, MF = 67 mmol.
[h] Conversion of DMM to monomeric formaldehyde, i.e., $X_{HCHO,DMM}$.
[i] Conversion of DMM to $C_{(s)}$ (measured as water less DME plus MG and monomeric HCHO).
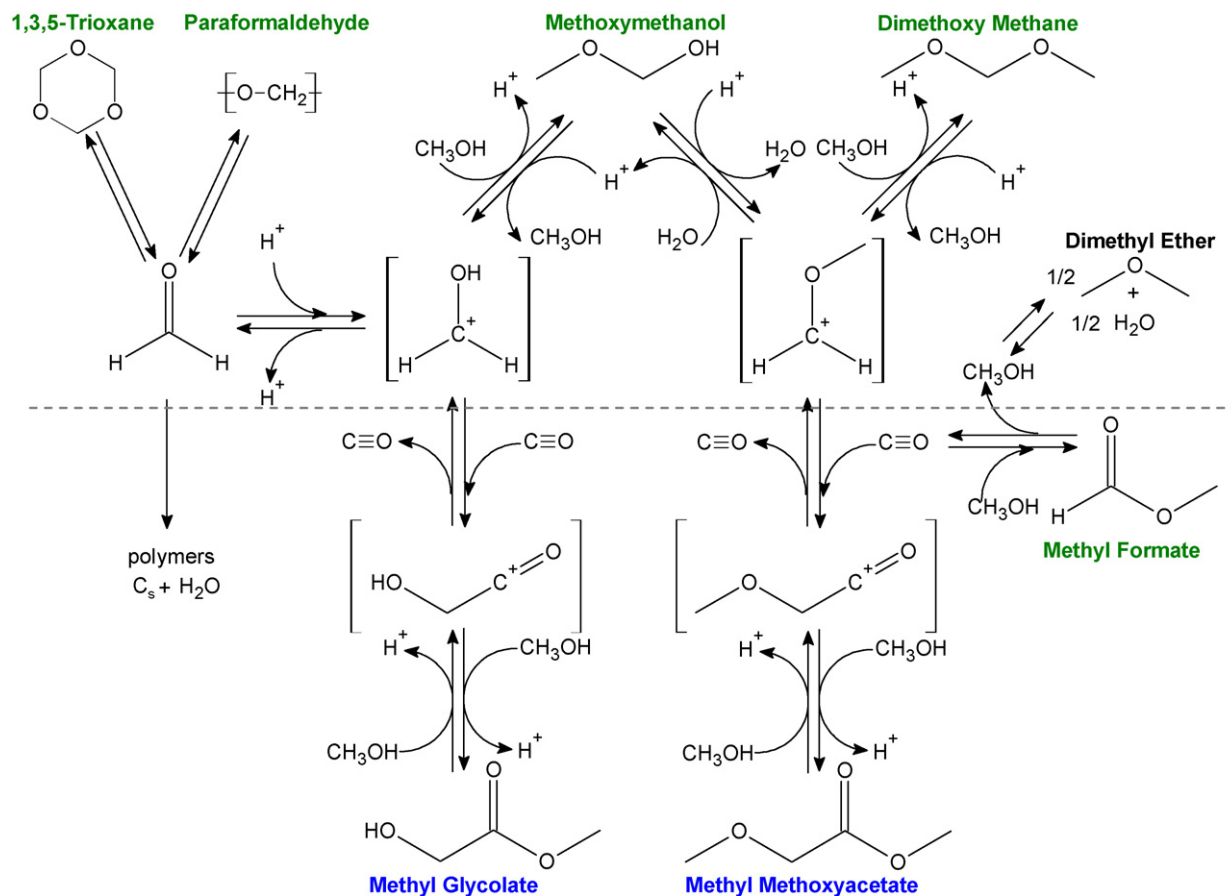
Fig. 12. Proposed reaction scheme. Steps above the dotted line are considered to be in equilibrium, and the steps below the line are considered kinetically limited.

accounted for in this way excludes water produced from the formation of DMM, DME, and MMAc.) Since all four formaldehyde source systems generated different CO pressures, the conversion of the generated CO to C_2 products is also given. It is evident that the highest conversion of formaldehyde to C_2 products is achieved using 1,3,5-trioxane as the formaldehyde source and the lowest conversion to these products is achieved using methoxymethanol. This is attributed to the effect of solvent leveling when methanol and water are present at short reaction times, reducing the acidity of the system and thus limiting the amount of CO released from MF. When using 1,3,5-trioxane, no methanol was added, and the formaldehyde source was anhydrous (unlike paraformaldehyde), so no protic solvents were present at short reaction times, and the highest CO pressures were reached of all the formaldehyde sources used. Although DMM is also anhydrous, and no methanol was added, methanol was released by reaction with the acid catalyst. Another interesting observation is that the conversion to carbon is lower when excess methanol is present, e.g., when using methoxymethanol, though this may be because the concentration of formaldehyde is lower in this case.

3.6. Proposed reaction scheme

The reaction scheme in Fig. 12 is proposed as a means of relating observable products to reactants. The first step when either paraformaldehyde or 1,3,5-trioxane is used as a reactant is the generation of formaldehyde in solution. In the next step, the substrate is protonated to generate a carbocation. Protonation of monomeric formaldehyde yields a hydroxycarbocation, while protonation of DMM yields a methoxycarbocation via loss of methanol.

Protonation of methoxymethanol produces either the hydroxycarbocation via loss of methanol or the methoxycarbocation via loss of water. If water and methanol are both present, interconversion of the two carbocations via methoxymethanol occurs readily. Since DMM formation from formaldehyde was observed to occur rapidly, formaldehyde, DMM, and methoxymethanol are assumed to reach equilibrium rapidly once heated to the reaction temperature. Therefore the concentration of water and methanol determines the distribution of these C_1 formaldehyde sources, as well as the relative abundance of the hydroxy- and methoxycarbocations. The reactions between formaldehyde sources and carbocation intermediates are rapid and, hence, are very likely to be at equilibrium. Therefore, for this reason all of the processes above the dotted line in Fig. 12 and are considered equilibrated.

Reaction of the hydroxy- and methoxycarbocations with CO leads to two resonance-stabilized acyl carbocations. Addition of methanol to the carbonylation product of the hydroxycarbocation leads to MG. (Addition of water leads to a small amount of glycolic acid, not shown). The carbonylation of the methoxycarbocation leads to MMAc after methanol addition. (Addition of water would lead to methoxyacetic acid, not shown.) The selectivities to MG and MMAc of the formaldehyde sources studied here are thought to reflect the relative abundance of the hydroxy- and methoxycarbocations, which themselves depend on the concentrations of water and methanol.

Paraformaldehyde and 1,3,5-trioxane are shown as the sources of monomeric formaldehyde from which the hydroxy- and methoxycarbocation intermediates are formed. However, the scheme also shows how DMM and methoxymethanol can also gen-
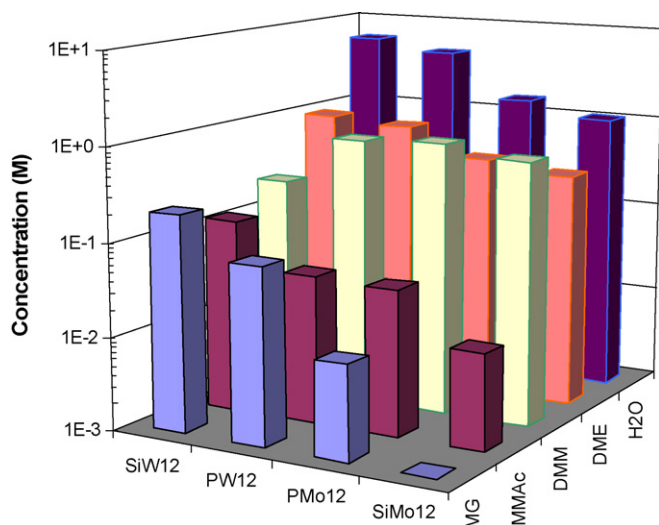
Fig. 13. Comparison of heteropoly acids on an equal catalyst mass basis using paraformaldehyde as the formaldehyde source. Time = 3 h, T = 150 °C, 0.25 g catalyst, HCHO = 67 mmol as paraformaldehyde, CH_3OH = 16 mmol, MF = 67 mmol.

Table 2

Comparison of SiW_{12}, PW_{12}, and methanesulfonic acid on an equimolar acid basis using paraformaldehyde as the formaldehyde source

Concentration (M)	SiW_{12}	PW_{12}	CH_3SO_3H
MG	0.21	0.10	0.00
MMAc	0.12	0.06	0.00
DMM	0.94	0.49	1.2
H_2O	6.0	7.8	1.0

Time = 3 h, T = 150 °C, 0.35 mmol H^+, HCHO = 67 mmol as paraformaldehyde, CH_3OH = 16 mmol, MF = 67 mmol.

erate the same carbocations, thereby undergoing carbonylation as well.

The scheme shows the decomposition of MF as the CO source. The slow release of CO from MF limits the carbonylation rate, and therefore the formation of C_2 compounds. However, as MF is also a source of methanol, slow methanol release also limits DMM formation, enabling C_2 product concentrations to rise to a greater level. The formation of byproduct polymers and carbonization are shown as being formed from monomeric formaldehyde, although the true mechanism for this process is not understood. The carbonylation step, CO release from MF, and polymer and carbon formation reactions are all represented below the dotted line in Fig. 12, indicating that they are kinetically relevant, in contrast with the equilibrated steps above the dotted line.

From Fig. 12, it is apparent that the rate of formation of C_2 products would be enhanced if CO release from MF and CO incorporation into products occurred at faster rates. However, the rate of CO release has been shown to be slow, especially with respect to DMM formation from formaldehyde. High-CO pressures were found to lead to higher C_2 product concentrations, as would be predicted from the scheme. It can also be seen that high-methanol concentrations would lead to increased DMM formation.

The product solutions obtained using paraformaldehyde as the source of formaldehyde were generally darker than those using 1,3,5-trioxane. It is also not apparent why solutions generated from DMM were almost colorless, yet resulted in larger amounts of solid collected. It is clear, however, that low concentrations of methanol contributed to both darker solutions and more solid being collected. This suggests that keeping the formaldehyde concentration low by including a solvent such as methanol may help to reduce the rates of unwanted byproduct formation.

3.7. Role of the catalyst

In the preceding discussion, the catalyst was treated solely as a proton source, and the role of the heteropolyanion was ignored. To determine whether the composition of the anion affects the catalyst activity, several heteropoly acids were examined.

The performance of SiW_{12}, PW_{12}, $SiMo_{12}$, and PMo_{12} in the carbonylation of paraformaldehyde were compared (Fig. 13), using

0.25 g of catalyst in each experiment. The molybdic acids gave low combined yields of MG and MMAc compared to the tungstic acids. This is attributed to the greater reducibility of the molybdic acids [17,23]. Since reduced HPAs are more basic [23], their effectiveness as acid catalysts is diminished. Reduction of the HPA during reaction was evidenced by the blue color of post-reaction solutions containing $SiMo_{12}$ and PMo_{12}, indicating the formation of reduced "heteropoly blues." The composition of the reducing agent is not known, but both methanol and formaldehyde could serve this purpose. The selectivity to MG and MMAc reversed for the tungstic and molybdic acids; both SiW_{12} and PW_{12} were more selective to MG, whereas $SiMo_{12}$ and PMo_{12} were more selective to MMAc.

The difference between SiW_{12} and PW_{12} acids may be partially explained by differing number of protons—four in SiW_{12}, and three in PW_{12}. Starting with equivalent numbers of protons (Table 2), SiW_{12} still gave a higher concentration of MG and MMAc than PMo_{12}. In contrast to HPAs, methanesulfonic acid (CH_3SO_3H), a typical strong liquid acid, produced only DMM and no C_2 products.

The relative activity of SiW_{12} cannot be explained by acid strength alone. Common measures of acid strength in heteropoly acids place them in the order $PW_{12} > SiW_{12} \geq PMo_{12} > SiMo_{12}$ [23,24], although depending on the method used, the differences between the last three can be quite small or none at all [24]. However, the superior acid strength of PW_{12} is reproduced in almost all cases. Both Fig. 13 and Table 2 show that C_2 production was greater for SiW_{12} than for PW_{12}. Methanesulfonic acid is a weaker acid than either of the heteropoly acids, but not so much weaker as to explain the lack of any detectable C_2 compounds from the reaction.

He et al. [17] have attributed the difference in reactivity between SiW_{12} and PW_{12} to the softness of the soft heteropoly anion formed from deprotonation of the parent acid, stating that it helped form a carbanion by deprotonating MF. Formation of a carbanion under acidic conditions is not usually possible, though the softness of the heteropoly anion most likely plays an important role in the catalysis. Izumi et al. [25] have investigated the cleavage of ethers catalyzed by heteropoly acids. The authors noted that in some cases SiW_{12} exhibited higher reactivity than PW_{12}, and attributed this difference to stabilization of the intermediate carbocations by the soft heteropoly anion base. In their study, equilibrium constants for formation of silver salts of heteropoly anions were two orders of magnitude larger for SiW_{12} than for PW_{12}, which were in turn one order of magnitude larger than those of either PMo_{12} or $SiMo_{12}$. Increased stabilization of soft carbocation intermediates through soft acid-soft base interactions could explain why SiW_{12}, while a weaker acid than PW_{12}, was a more effective carbonylation catalyst as seen in this study. It could also explain why methanesulfonic acid, which produces the hardest conjugate base amongst acids considered here, would produce no carbonylation products at equal molar proton loadings to the heteropoly acids.

If the interaction of the carbocation and the heteropoly anion is considered as a coordinative interaction, a reaction mechanism can be proposed similar to Fig. 14. In the mechanism, formaldehyde is
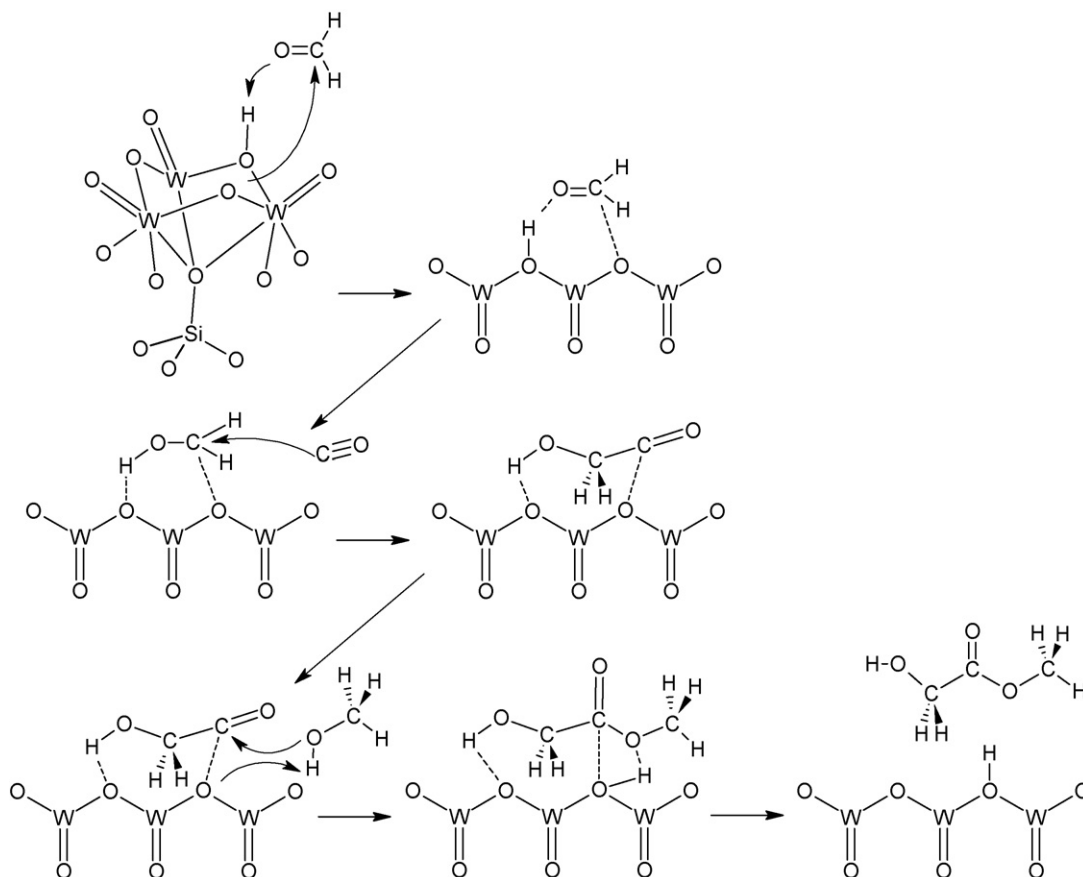
Fig. 14. Proposed reaction mechanism for the carbonylation of free formaldehyde to methyl glycolate. The heteropoly acid Keggin unit has been simplified, first by considering one trimetallic cluster, and then representing that cluster linearly.

carbonylated to form a carbocation stabilized by its coordination to the heteropoly acid. Carbon monoxide addition then takes place, forming a stabilized acyl carbocation, followed by reaction with methanol, releasing the product MG and regenerating the acidic proton. The function of the catalyst is purely as a Brønsted acid/soft base. The heteropoly acids considered here do not possess any Lewis acidity [24]. As such, CO has no sites to coordinate to prior to reaction with protonated formaldehyde, and CO insertion occurs by an Eley-Rideal mechanism. This may limit the rate at which CO insertion occurs.

As formaldehyde is proposed to be in equilibrium with methoxymethanol, DMM, and the hydroxy- and methoxycarbocation intermediates shown in the reaction scheme (Fig. 12), the stabilization of these carbocations is not likely to be important in explaining the difference in activity between SiW_{12} and PW_{12}. The stabilization of the acyl carbocations formed after CO addition is therefore proposed to be the distinguishing effect between the activity of SiW_{12} and PW_{12}.

4. Conclusions

The acid-catalyzed carbonylation of formaldehyde by MF produces MG and MMAc. These products, referred to as C_2 compounds, are precursors to ethylene glycol. DME, DMM, and a carbonaceous solid are the main byproducts. The selectivity to C_2 compounds is strongly influenced by the source of formaldehyde and the concentration of methanol in the reaction system. Methoxymethanol in methanol solution gave the lowest yields of C_2 products due to the large excess of methanol, which reacted to form DME and DMM. Paraformaldehyde required only a small amount of methanol to

prevent polyoxymethylene formation, and gave a greater yield of C_2 products. 1,3,5-Trioxane required no additional methanol, resulting in the highest yield of C_2 products. C_2 yields from DMM were intermediate between those for paraformaldehyde and 1,3,5-trioxane. DMM was also found to undergo carbonylation by gas-phase CO more readily than paraformaldehyde.

Slow release of CO from MF was identified as the primary factor limiting the rate of formaldehyde carbonylation. High concentrations of methanol decreased the rate of CO release from MF. Introduction of modest amounts of CO into the gas phase gave more than proportional increases in C_2 products by increasing the availability of CO at short reaction times.

A reaction scheme was proposed to illustrate the relationships between reactants, products, and possible reaction intermediates. Formaldehyde, methoxymethanol, and DMM are taken to be in equilibrium with each other and with hydroxy- and methoxy-carbocations of formaldehyde. The relative abundance of these species depends on the concentrations of methanol and water. Carbonylation of the carbocation intermediates is thought to be the rate-limiting step in the formation of C_2 compounds, a process that is further limited by the release of CO from MF. The carbocation intermediates can also participate in the formation of carbonaceous deposits; hence, high-CO partial pressures are required to increase the yield of C_2 compounds and minimize the formation of carbon.

The activities of common heteropoly acids were compared with each other and with the activity of methanesulfonic acid for similar acid loadings. Methanesulfonic acid, a strong acid with a hard counter anion, yielded no C_2 compounds, whereas the heteropoly acids, which are strong acids with soft counter anions, produced C_2 compounds. It is proposed that soft anions are responsible for

stabilizing the acyl carbocations formed after CO addition to the protonated formaldehyde. High activity was also found to correlate with resistance of the anion to reduction.

Acknowledgements

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