Poly(4-vinylpyridine) catalyzed selective methanolysis of methyl and methylene bromides

G. K. Surya Prakash [a,*], Juan C. Colmenares [a,b,†], Patrice T. Batamack [a], Thomas Mathew [a], George A. Olah [a,*]

[a] *Department of Chemistry, University of Southern California, Loker Hydrocarbon Research Institute, USC, 837 Bloom Walk, Los Angeles, CA 90089-1661, USA*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01224 Warsaw, Poland*

ABSTRACT

The effect of poly(4-vinylpyridine) (PVP) on the methanolysis of methyl bromide and methylene bromide was studied at temperatures between 75 °C and 125 °C. PVP acts as an efficient HBr scavenger promoting the formation of dimethyl ether (DME) and dimethoxymethane (DMM) from the corresponding bromom- ethanes and methanol in moderate yields with high selectivity. No reaction was observed in the absence of PVP under the conditions adopted. The activity of the catalyst remained unchanged even after five cycles showing the efficacy and application of the polymer as an environmentally green reagent as well as catalyst in this methanolysis reaction.

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Dimethyl ether (DME) and dimethoxymethane (DMM) are two important chemicals in the area of fuels and energy sources be- cause of their attractiveness as promising additives and/or alterna- tives to diesel fuels. DME possesses many physical and chemical properties suitable for its development as an environmentally safe and efficient fuel.[1–4] DME is not corrosive, nor carcinogenic and does not form peroxides upon prolonged exposure to air. DME is a suitable substitute for the CFC ozone depleting gases used as aer- osol propellants, a precursor for the production of dimethyl sulfate and a potential building block of a variety of chemicals. As a poten- tial diesel fuel, DME has a cetane number higher than regular diesel fuel, a good heating value (42.5 MJ/kg), a vapor pressure of 5.1 bar at 20 °C allowing its handling as a Liquefied Petroleum Gas (LPG). The thermal efficiency and the soot free CO_x/hydrocarbons emis- sions of DME are equivalent to that of diesel at all loads. Lower nitrogen oxide emissions, injection pressures, and engine noise are observed with the use of DME.[3]

DMM is an ideal solvent in pharmaceutical, perfumery, and painting industries due to its low toxicity and corrosiveness, strong dissolving power, low viscosity, good penetration, and high evapo- ration capacities. DMM is also used in the production of ion ex- change resins, polyacetals, and glue formulations.[5] DMM can be utilized as a potential additive for diesel. Diesel-DMM blends with the DMM fraction volume 0–50% retarded ignition delay, increased the efficiency of the diesel engine with a substantial reduction in smoke and CO_x and NO_x emissions.[6]

Both DME and DMM are derived from methanol (prepared from syn gas which in turn is obtained from methane by steam reforming). DME is obtained by the dehydration of methanol over an acid cata- lyst while DMM is produced from the condensation of methanol with formaldehyde at 150–180 °C and 10 bar. Research is underway to produce DME in a single step from syn gas[3,7,8] while oxidation of methanol over various solid catalysts is being investigated for the synthesis of DMM.[9] Bromination is one of the promising routes to functionalize methane at temperatures lower than those used for the steam reforming. High conversions and selectivity for methyl bromide and methylene bromide can be achieved around 600 °C.[10,11] In a previous paper,[12] we reported that methanol and DME could be efficiently produced from methyl bromide and water in the presence of poly(4-vinylpyridirne) (PVP). PVP acts as a catalyst and an acid scavenger with significant enhancement in the rate of hydrolysis while decreasing corrosion due to HBr. In continuation of our efforts to use PVP as a catalyst and to suppress corrosion dur- ing reactions using methyl halides, we now describe the methanol- ysis of methyl bromide and methylene bromide to DME and DMM, respectively.

Temperature plays a key role in the methanolysis of methyl bro- mide. The results of the methanolysis of methyl bromide between 75 °C and 125 °C in the presence and absence of PVP are shown in Table 1. At 75 °C, even in the presence of PVP and at a higher tem- perature (125 °C) in the absence of PVP, no reaction was observed.

* Corresponding author. Tel.: +1 213 740 5984 (G.K.S.P.).
E-mail addresses: gprakash@usc.edu (G.K. Surya Prakash), jcarlos@ichf.edu.pl, jcarlos@wp.pl (J.C. Colmenares).
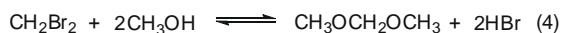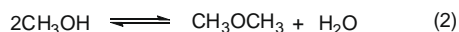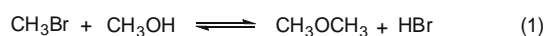† Fax: +48 22 6325276.

Table 1
Effect of PVP and temperature on the methanolysis of methyl bromide[a]

| Entry	Molar ratio ($CH_3OH:CH_3Br:PVP$)	Temperature (°C)	Conversion of CH_3Br (%)	Selectivity of DME (%)
1	3:3:1	75	None	None
2	3:3:1	100	24	100
3	3:3:1	125	35	100
4	3:3:0	125	None	None

[a] Reaction time 2 h.

However, in the presence of PVP, the conversion of methyl bromide at 100 °C and 125 °C was found to be 24% and 35%, respectively. The formation of DME via methanolysis of CH_3Br (Scheme 1, reaction 1) is a base-catalyzed reaction; the presence of PVP significantly enhances the rate of the reaction. Reaction 2 (which can also produce DME) is acid catalyzed and requires excess methanol. Since the amount of methanol is limited and the presence of PVP diminishes the effect of HBr as an acid catalyst, the formation of DME by methanol condensation is not significant. Therefore, reaction 1 is more dominant than reaction 2 under the reaction conditions (Scheme 1).

$$CH_3Br \ + \ CH_3OH \ \rightleftharpoons \ CH_3OCH_3 \ + \ HBr \qquad (1)$$

$$2CH_3OH \ \rightleftharpoons \ CH_3OCH_3 \ + \ H_2O \qquad (2)$$

$$PVP \ + \ HBr \ \rightleftharpoons \ PVPH^+ \ Br^- \qquad (3)$$

$$CH_2Br_2 \ + \ 2CH_3OH \ \rightleftharpoons \ CH_3OCH_2OCH_3 \ + \ 2HBr \qquad (4)$$

Scheme 1. Methanolysis of CH_3Br and CH_2Br_2.

In the presence of PVP at 100 °C and 125 °C, methanolysis of methylene bromide gave solely dimethoxymethane (DMM) in 25% and 58% conversions, respectively, according to reaction 4. Neutralization of HBr is depicted in reaction 3.

Methanolysis of methylene bromide was not observed at 75 °C or in the absence of the catalyst at 125 °C. Hine et al.,[13] during a mechanistic study of the alkoxylation reactions of methylene halides by deuterium exchange, found that methylene bromide does not react with sodium methoxide to a significant extent by α-elimination in methyl alcohol-d, and the intermediate bromomethyl methyl ether does not undergo deuterium exchange or follow an α-elimination mechanism. Therefore, the reaction of methylene bromide with sodium methoxide consists of two consecutive S_N2 reactions, or of an S_N2 reaction followed by an S_N1 reaction (reaction 5).

$$CH_2Br_2 \xrightarrow{CH_3O^-} CH_3OCH_2Br \xrightarrow{CH_3O^-} CH_3OCH_2OCH_3 \qquad (5)$$
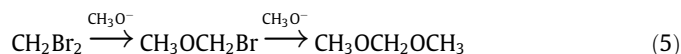
The higher conversion (58%) of methylene bromide at 125 °C can be attributed to the longer contact time of methylene bromide in the solution due to its higher boiling point (97 °C) compared to that of methyl bromide (3.6 °C), and the excess of methanol used.

In order to explore the possibility of recycling PVP in the methanolysis of the methyl bromides, the recovered polymer was tested over five cycles. The results are shown in Figure 1. It can be seen that the activity of PVP remained almost constant.

The SEM images (Fig. 2) show the surface morphology of fresh PVP before the reaction and recycled PVP regenerated after the 5th cycle. As can be seen, the surface morphology of PVP remains the same even after the 5th cycle confirming the stability of the polymer under the reaction conditions.

In conclusion, methyl bromide and methylene bromide, in the presence of methanol, have been efficiently and selectively converted into dimethyl ether and dimethoxymethane, respectively, over a basic solid polymer catalyst, poly(4-vinylpyridine), at moderate temperatures and pressures. At 125 °C and 8 bar, the yield of dimethyl ether was 35% and that of dimethoxymethane was 58%. The catalyst was reusable and maintained its activity after five cycles. With its ability to catalyze the methanolysis and to neutralize HBr, corrosion is virtually eliminated. This new method therefore proves to be practical for the preparation of ethers and acetals. More reaction–regeneration cycles are needed for a better evaluation of the stability of the catalyst.
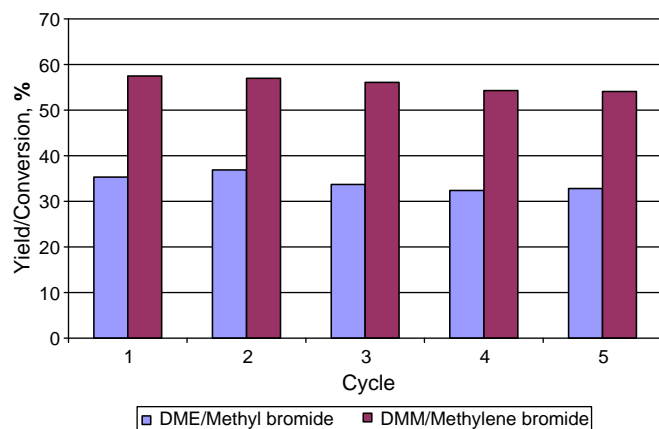

Figure 1. Study of the recyclability of PVP in the methanolysis of methyl and methylene bromide. Reaction conditions: 125 °C, 2 h reaction, molar ratio MeOH:CH_3Br:PVP = 3:3:1 and MeOH:CH_2Br_2:PVP = 4:1:1.
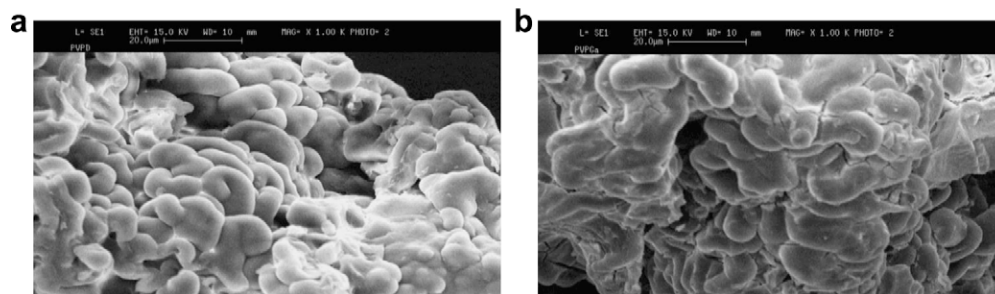

Figure 2. Surface morphology of PVP (SEM, 1000× magnification): (a) fresh sample of PVP, (b) recycled PVP (after the 5th cycle).

Table 2
Effect of PVP and temperature on methanolysis of methylene bromide[a]

Entry	Molar ratio (MeOH:CH$_2$Br$_2$:PVP)	Temperature (°C)	Conversion of CH$_2$Br$_2$ (%)	Selectivity of DMM (%)
1	4:1:1	75	None	None
2	4:1:1	100	25	100
3	4:1:1	125	58	100
4	4:1:0	125	None	None

[a] Reaction time 2 h.

PVP (MW is indefinite because of cross-linking) 2% cross-linked with divinyl benzene having a surface area of 17 m^2/g and a particle size of ∼60 mesh was used for the reactions. The basicity of PVP, pK_a ≈ 4.08, has been estimated from Refs. 14 and 15.

The methanolysis of methyl and methylene bromide was carried out in a closed pressure tube (internal volume, 20 mL). In a typical experiment, PVP (0.17 g) was added to a pressure tube followed by the addition of methanol (0.14 g, 4.38 mmol) and then sealed. Then, at room temperature, the tube was pressurized to 5.5 bar with methyl bromide and heated to 125 °C for 2 h under stirring (600 rpm). The mixture was then cooled to room temperature. The gas phase (unreacted methyl bromide and dimethyl ether) was collected by absorption in CDCl$_3$ solution kept at −50 °C (dry ice-acetone bath). The reaction mixture was washed several times with CDCl$_3$ and the solution was collected each time after filtration. In the case of CH$_2$Br$_2$ methanolysis, methanol (0.21 g, 6.56 mmol) was added to methylene bromide (0.28 g, 1.61 mmol) along with PVP (0.17 g) and the reaction was conducted under the conditions mentioned in Table 2. After each run, the reaction mixture was cooled to room temperature and PVP was separated from the mixture by filtration. All the products were characterized and analyzed by ^{1}H and ^{13}C NMR spectroscopy.

After each cycle, PVP was filtered and washed with CH$_2$Cl$_2$ (3 times) and H$_2$O (3 times) and then dried overnight at 100 °C under vacuum. The surface morphology of fresh and recycled PVP (after five consecutive reactions) was investigated by means of a scanning electron microscopy (SEM Cambridge 360, 3.0 nm resolution).

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