Poly(4-vinylpyridine) catalyzed hydrolysis of methyl bromide to methanol and dimethyl ether

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ARTICLE INFO

ABSTRACT

The hydrolysis of methyl bromide with neutral water is performed in the presence and absence of various amines in a batch reactor at different temperatures (50–125 °C). Screening of poly(4-vinylpyridine) as a potential reusable solid amine catalyst showed maximum efficiency. This significant enhancement in efficiency is due to the capture of HBr by solid PVP and remains phase-separated driving the reaction forward. The major advantage of this process is that the polymer can be easily regenerated and reused without loss of activity making it a very effective catalyst for the conversion of methyl halides to methanol and dimethyl ether.

1. Introduction

In the present context of global energy challenges and climatic changes, increase of energy demand and continuing depletion of oil reserves, natural gas should be utilized effectively as efficient source of energy and chemicals [1]. Methane, the major component of natural gas can be used to produce methanol, a good fuel and a vital building block for a large variety of compounds in the chemical industry [2]. In comparison with other routes to methanol which include the costly and highly energy consuming steam reforming of methane to the synthesis gas (syngas, CO/H$_2$), bromination of methane is considered very promising. At low temperatures, the selectivity to methyl bromide is almost 100%, but the conversion is low [3,4]. High conversions and selectivity to methyl bromide are obtained at temperatures between 500 °C and 700 °C [5,6]. The alkyl bromides can be directly converted to higher hydrocarbons over zeolites [7–10,5] or AlBr$_3$ [11] and to acetic acid via carbonylation and hydrolysis [12]. Methyl bromide yielded dimethyl ether and methyl acetate via oxidative carbonylation with CO and Cu$_2$O at 210 °C using SbF$_5$/graphite as catalyst [13] or methyl alcohol/dimethyl ether over metal oxides [14–16]. Catalytic hydrolysis of methyl bromide in a flow reactor over γ-Al$_2$O$_3$ at 375 °C gave methyl alcohol (73%) and dimethyl ether (27%) with 23% conversion [3]. Alkali and/or alkaline earth metal supported on activated carbon were also used for the hydrolysis of alkyl monohalides [17]. Methyl bromide has been used as an agricultural soil and structural fumigant to control a wide variety of pests. However, it depletes the stratospheric ozone layer and is classified as a Class-I-ozone-depleting substance. Several studies have focused on the natural production and consumption of methyl bromide in natural waters [18,19] and its hydrolysis catalyzed by activated carbons in contained environments, such as chambers, rooms, storehouses, ships, and mills [20] or by photoexcitation [21]. It was found that the hydrolysis of methyl bromide is too fast and therefore not economical compared to other chlorofluorocarbons used as agents in the hydrate process for water desalination [22].

Studies of the kinetics of the uncatalyzed hydrolysis of methyl halides showed that the order of ease of hydrolysis is: CH$_3$Br > CH$_3$I > CH$_3$Cl [23–25]. The magnitudes of the rate constants indicated a mechanism intermediate between the classical SN1 and SN2 types. In the presence of the hydroxyl ions this order is changed as follows: CH$_3$I > CH$_3$Br > CH$_3$Cl [26]. The enthalpies of activation for the hydrolysis of methyl bromide at 25 and 100 °C are 25.3 and 21.8 kcal/mol, respectively [25]. The half-life of methyl bromide hydrolysis at 25 °C, 21 days is reduced to about 5 days at 35 °C [27]. In disagreement with the above order of hydrolysis,

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the study of the initial-state and transition-state isotope effects of methyl halides in light and heavy water showed that CH_3Cl is more ionized than CH_3Br at the transition state during solvolysis in water at 40–70 °C [28]. According to Albery and Curran [29], the solvent isotope effect on the solvolysis of methyl bromide in mixtures of H_2O and D_2O is separated into two contributions, one the effect of attacking nucleophile and the other that of the medium associated with the developing Br^-. The effect of pressure on the rate of hydrolysis of methyl bromide showed that the high-pressure mechanism has perhaps more covalent attachment of water in the transition state, making it more $SN2$-like, than the low-pressure mechanism [30]. The transition state in the hydrolysis of methyl bromide is examined in more details using the Marcus theory in the study of the transfer of the methyl group in $SN2$ reactions [31]. Using the flowing-afterglow technique, a technique capable of producing solvated ions in the gas phase and allowing close examination, in a quantitative manner, the transition in the kinetics and energetics of ion-molecule reaction from their solvent-free behavior to that observed in solution, and the absolute influence of solvent on such reactions can be deduced as

$$OH^- \cdot (H_2O)_n + CH_3Br \rightarrow Br^- \cdot (H_2O)_n + CH_3OH$$
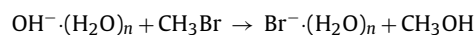
the rate of the reaction is seen to decrease progressively with the stepwise addition of water vapor molecules up to $n = 3$, a value which represents the present operational limit of the technique [32].

Amines such as triethylammonium hydroxide and piperidine have been suggested as catalysts for the hydrolysis of alkyl halides [8] and many tertiary amines were studied for their ability to remove hydrogen halide from organic halides to form unsaturated compounds [33]. Poly(4-vinylpyridine) (PVP) can coordinate with a large number of HF molecules to form a complex which can be used as an environmentally friendly catalyst for the alkylation of isobutane with butenes to produce alkylates of high octane numbers [34]. To our best knowledge, PVP has not yet been tested as both a catalyst and an acid scavenger in the hydrolysis of alkyl halides. Herein, we disclose the great potential of the solid poly(4-vinylpyridine) as environmentally friendly reusable catalyst in the hydrolysis of methyl bromide acting as an efficient HBr scavenger.
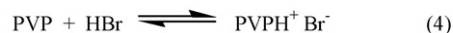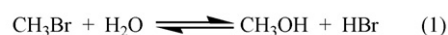
2. Experimental

2.1. Reagents

All reagents were supplied by Aldrich and used as received. Methyl bromide with 99.5% purity and Milli-Q quality water were used. All the reactions were conducted with 2% cross-linked PVP (with divinylbenzene) with a surface area of 17 m^2/g.

2.2. General experimental procedures

The hydrolysis of methyl bromide was performed in a 20 mL glass pressure tube. In a typical experiment, about 0.17 g of PVP was loaded in the tube followed by addition of 0.82 g of water. The tube was then pressurized to 5.5 atm with methyl bromide and heated under vigorous stirring at the required temperature for the specified period of time. After this time, the tube was cooled down to room temperature. The gas phase was collected in a CDCl$_3$ solution maintained at -50 °C. The content of tube was washed several times with CDCl$_3$ and the solution was collected each time after filtration. For liquid amines, gas phase was collected in the same way as above, and the remained liquid in the tube was analyzed directly. The products were analyzed by ^{1}H and ^{13}C NMR on a Varian Mercury-400 NMR spectrometer and quantified using dichloromethane as internal standard. Apart from methanol and dimethyl ether, there were not other products detected.

$$CH_3Br + H_2O \rightleftharpoons CH_3OH + HBr \quad (1)$$

$$CH_3OH + CH_3Br \rightleftharpoons CH_3OCH_3 + HBr \quad (2)$$

$$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad (3)$$

$$PVP + HBr \rightleftharpoons PVPH^+ Br^- \quad (4)$$

Scheme 1. Plausible reactions during the hydrolysis of methyl bromide.

Table 1
Effect of the molar ratio of CH$_3$Br:PVP on the hydrolysis of methyl bromide.[a]

Entry	Molar ratio (CH$_3$Br:PVP)	Conversion of CH$_3$Br (%)	Selectivity (%)	
			DME	MeOH
1	1:0	29.9	48.4	51.6
2	1:0.125	67.2	59.8	40.2
3	1:0.2	87.6	43.0	57.0
4	1:0.33	86.8	30.0	70.0
5	1:1	85.6	29.0	71.0

[a] Reaction conditions: 2 h at 100 °C with H$_2$O:CH$_3$Br molar ratio of 10:1.

Table 2
Effect of temperature on the hydrolysis of methyl bromide.[a]

Entry	Temperature (°C)	Conversion of CH$_3$Br (%)	Selectivity (%)	
			DME	MeOH
1	50	51.9	100.0	0.0
2	75	63.7	78.4	21.6
3	100	86.8	30.0	70.0
4	125	68.4	62.7	37.3

[a] Reaction conditions: 2 h with H$_2$O:CH$_3$Br:PVP molar ratio of 30:3:1.

Table 3
Effect of molar ratio of H$_2$O:CH$_3$Br:PVP on the hydrolysis of methyl bromide.[a]

Entry	Molar ratio H$_2$O:CH$_3$Br:PVP	Conversion of CH$_3$Br (%)	Selectivity (%)	
			DME	MeOH
1	15:3:1	69.3	51.1	48.9
2	30:3:1	86.8	30.0	70.0

[a] Reaction conditions: 2 h, 100 °C.

2.3. PVP regeneration

Before reuse, PVP was filtered and washed with dichloromethane (3×) and water (3×) and dried at 100 °C overnight in vacuum.

3. Results and discussion

The hydrolysis of methyl bromide proceeds as shown in Eq. (1). Dimethyl ether (DME) is also observed in the reaction products as a result of the condensation of methanol (MeOH) and methyl bromide (Scheme 1, Eq. (2)) or that of two molecules of methanol (Scheme 1, Eq. (3)). The neutralization of HBr with PVP is materialized by Eq. (4). Various factors influencing the conversion and selectivity were studied and the results are shown in Tables 1–4.

3.1. Influence of the CH$_3$Br:PVP molar ratio

Table 1 shows the results detailing the effect of PVP and CH$_3$Br:PVP molar ratio on the hydrolysis of methyl bromide at a constant molar ratio of H$_2$O:CH$_3$Br = 10:1. The change in the CH$_3$Br:PVP ratio from 1:0 to 1:1 influenced both the conversion of CH$_3$Br and the selectivity to DME and MeOH. The conversion of methyl bromide gradually increased from 30% in the absence of PVP to 87.6%

Table 4
Effect of different amines on the hydrolysis of methyl bromide.[a]

Entry	Amine	pK_a [35]	Conversion of CH$_3$Br (%)	Selectivity (%)	
				DME	MeOH
1	PVP	4.08[b]	86.8	30.0	70.0
2	Pyridine	5.23	57.4	45.1	54.9
3	Pyridine[c]	5.23	53.6	100.0	0.0
4	Pyridine[d]	5.23	80	42.0	58.0
5	4-Ethylpyridine	5.99	56.8	40.6	59.4
6	4-Isopropylpyridine	6.03	46.3	55.0	45.0
7	2-Methoxypyridine	3.25	42.0	40.0	60.0

[a] Reaction conditions: 100 °C for 2 h with H$_2$O:CH$_3$Br:amine molar ratio of 30:3:1.
[b] Estimated from Refs. [36,35].
[c] Reaction temperature 50 °C.
[d] With H$_2$O:CH$_3$Br:pyridine molar ratio of 10:1:1.

when the ratio CH$_3$Br:PVP was 1:0.2 then remained almost constant above. Catalytic addition of PVP produced a 2.2-fold increase in the methyl bromide conversion (entry 2). Approximately three-fold enhancement in conversion was observed with CH$_3$Br:PVP ratio 1:0.2. As a weak base [35,36], small amount of PVP will produce excess OH$^-$ anions in water and catalyze the hydrolysis of methyl halides [23–25]. Addition of more base above the ratio CH$_3$Br:PVP 1:0.2 did not improve the conversion of CH$_3$Br though significantly altered the selectivity of the reaction. The formation of DME was decreased. Reactions (1) and (2) are catalyzed by a base while reaction (3) is acid catalyzed. More PVP will be effective in lowering the rate of reaction (3) by decreasing the overall acidity in the medium through HBr capture by PVP. Hence, a decrease in the yield and selectivity of DME may be explained by (a) the rate decline for reaction (3) due to decrease in acidity and (b) the rate decline for reaction (2) due to decrease of basic sites of PVP catalyst owing to HBr association.

3.2. Influence of the temperature

The influence of the temperature on the hydrolysis of CH$_3$Br using PVP has been also studied (Table 2). When the temperature of the reaction (with H$_2$O:CH$_3$Br:PVP ratio 30:3:1) was increased from 50 to 100 °C, the conversion was increased from 52% to 87% with a sharp enhancement in selectivity of methanol. However, the selectivity of DME declined from 100% to 30%. Further increase in temperature to 125 °C decreases the conversion of CH$_3$Br (68%) as well as the selectivity of methanol (37%). Since the boiling point of CH$_3$Br is low (3.6 °C), low temperatures along with the pressure built up lead to long contact times of methyl bromide in water and improve the selectivity of DME while penalizing the conversion
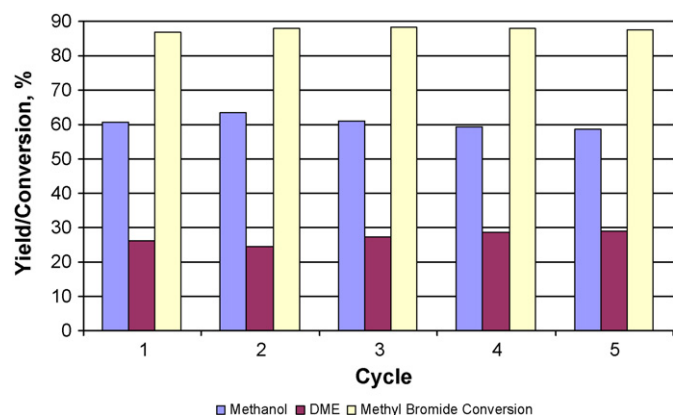
because of the energy barrier [23–25]. On the other hand, high temperatures will favour high conversion of CH$_3$Br and adversely affect the selectivity to DME. But if the temperature is too high, at 125 °C, above the boiling of water, gas phase reactions might predominate reducing the conversion of methyl bromide and improving the selectivity of DME because of the readily available of HBr in gas phase.

3.3. Influence of the dilution

Amount of water plays a significant role in hydrolysis. The effect of the dilution is presented in Table 3. By increasing the amount of water, the conversion of methyl bromide increased and the selectivity to methanol has been enhanced as expected.

3.4. Comparison of PVP with other amines

Liquid pyridine derivatives of different basic strength were studied and compared with that of PVP. The results are shown in Table 4. Despite the homogeneous nature of the reaction with liquid amines, PVP exhibited a higher conversion to methyl bromide and a better selectivity to methanol. No direct correlation was found between the strength of the base and the conversion or the selectivity. 4-Isopropylpyridine, the strongest base in the series did not yield a high conversion of CH$_3$Br. The selectivity to DME is slightly increased with liquid amines. At 50 °C, pyridine and PVP show similar catalytic activity and selectivity. More pyridine was necessary (entry 4, CH$_3$Br:pyridine, 1:1) in order to obtain a conversion level of CH$_3$Br close to that of PVP (CH$_3$Br:PVP, 1:0.33).

3.5. Recycling of PVP

Catalytic activity of PVP was tested over five cycles. All these reactions were carried out at 100 °C, for 2 h with H$_2$O:CH$_3$Br:PVP molar ratio of 30:3:1. The polymer showed no sign of deactivation after five consecutive runs (Fig. 1). The conversion and the selectivity remained almost constant. We found that the poly(4-vinyl pyridinium bromide) can be oxidized in an aqueous solution of H$_2$O$_2$ and the bromine after filtration recovered by heating. Bromine can be recycled to produce methyl bromide with methane.

4. Conclusion

The hydrolysis of methyl bromide was efficiently catalyzed in the presence of poly(4-vinyl pyridine) in a batch reactor at moderate pressures yielding methanol and dimethyl ether. Many factors including the ratios H$_2$O:CH$_3$Br:PVP and the temperature affect both the conversion and the selectivity. The reaction conditions can be adjusted to either obtain solely dimethyl ether or both products in a desired ratio. At 50 °C, only DME is obtained which is one of the major achievements of these studies because of the growing importance of DME as a biofuel [2,37]. At higher temperatures, the conversion of methyl bromide is increased and the selectivity depends on the temperature. Above 50 °C, PVP was shown to be a better base than other liquid pyridine derivatives. At 100 °C, the conversion of CH$_3$Br was 87% and the selectivity to DME 30%. As a solid, PVP has also others advantages: the products can be easily collected from the reaction medium and the regeneration of the polymer is facile. One of the major problems associated with the hydrolysis of organic halides is corrosion. The use of PVP instead of a liquid amine will significantly decrease corrosion. Adding that PVP can be easily disposed of, the hydrolysis of organic halides using this base is not only efficient but also highly environmentally friendly and therefore industrially economically feasible. The hydrolysis of methylene bromide failed to produce formaldehyde under the conditions used.

Fig. 1. Recycling of PVP for successive hydrolysis of methyl bromide.

Acknowledgment

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