J. Chem. Tech. Biotechnol. 1979, **29**, 433–436

Studies on the Preparation of Methyl Bromide from Sulphur, Bromine and Methyl Alcohol

Haiderali M. Bhavnagary, Tirunillai S. Krishnamurthy and Suvendu K. Majumder

Discipline of Infestation Control and Pesticides, Central Food Technological Research Institute, Mysore–570013 India

(Paper received 30 August 1978 and accepted 14 February 1979)

Optimum conditions have been presented for the production of methyl bromide by employing the reactants, sulphur, methyl alcohol, liquid bromine and water. For the maximum recovery of methyl bromide from liquid bromine used in the reaction, a 5% excess of sulphur and 30% excess of water than the stoichiometric quantities were found necessary. The addition of liquid bromine to the reaction mixture at slower rates of 0.5 to 2.5 $cm^3\ min^{-1}$, reduced the loss of bromine as sulphur bromide and increased the yield of methyl bromide from 42 to 94.3%. With these standardised conditions, the product had a methyl bromide content of 98.2% with an overall yield of 94.42% based on liquid bromine.

1. Introduction

Methyl bromide has been employed extensively in recent years as a fumigant for the control of stored grain pests and various soil and plant pests. Methyl bromide is an irritant and a highly penetrative fumigant. The methyl bromide absorbed by the pests undergoes decomposition with the formation of inorganic bromide and a series of methylated derivatives.[1,2] Methyl bromide is a gas at ordinary temperature and pressure with a boiling point of 276.6 K and a density of 1.75 at 273 K. The low boiling point of methyl bromide makes it convenient for its separation from the bulk reaction mixture in a pure state. On a small scale it is prepared by the bromination of methane.[3] Earlier manufacturing methods include the action of sodium,[4] potassium, ammonium or iron bromide[5] on a mixture of methyl alcohol and sulphuric acid below 323 K. Gaseous hydrogen bromide or its aqueous solution[6,7] is also used in place of metal bromides to react with methyl alcohol in the presence of sulphuric acid as a catalyst. In a few of the earlier methods, red phosphorus[8,9] was employed as a reducing agent for bromine forming phosphorus bromide (PBr_3) which reacts with methyl alcohol to yield gaseous methyl bromide. The process utilising liquid bromine for its conversion to methyl bromide in presence of sulphur or sulphur dioxide as a reducing agent is connected with a number of patents and no experimental data are available in the literature.[10–13] Therefore, the present study was undertaken to standardise the optimum conditions for the preparation of methyl bromide using sulphur, liquid bromine and methyl alcohol. In the presence of water the overall reaction[14] could be presented by the following reaction:

$$3S + 9Br_2 + 12H_2O \rightarrow 18HBr + 3H_2SO_4 \qquad (1)$$

In the initial stage of this reaction sulphur reduces bromine forming sulphur bromide as

$$2S + Br_2 \rightarrow S_2Br_2 \qquad (2)$$

The sulphur bromide in turn reacts with water yielding hydrobromic and sulphuric acids. The hydrobromic acid so formed reacts with methyl alcohol at 343–353 K to yield methyl bromide and water.

2. Experimental

Experiments were carried out to study the effect of excess quantities of the reactants (Tables 1–3) on the yield of methyl bromide according to the chemical reaction (1). Experiments were also conducted with increasing quantities of reactants (Table 4) for assessing the quality and yield of methyl bromide. The quantities of reactants taken were as per the optimum requirements arrived at by the earlier experiments.

Table 1. Effect of excess quantity of sulphur as reducing agent on the formation of methyl bromide (temperature of reaction, 348 K; methyl alcohol, 120 cm^3; liquid bromine, 50 cm^3; water 22 cm^3)[a]

Weight of sulphur added (g)	Excess over the stoichiometric requirement (g)	Weight of methyl bromide obtained (g)	Yield of methyl bromide[b] (%)
10.00	0.0	146	80.23
10.25	2.5	151	83.00
10.50	5.0	155	85.30
10.75	7.5	156	85.85
11.00	10.0	155	85.30

[a] Theoretical requirement.
[b] Based on liquid bromine initially used.

Table 2. Effect of rate of addition of liquid bromine on the yield of methyl bromide (temperature of reaction, 348K; methyl alcohol, 120 cm^3; liquid bromine, 50 cm^3; sulphur, 10.5 g; water 28.5 cm^3)[a]

Rate of addition of liquid bromine (cm^3 min^{-1})	Weight of methyl bromide obtained (g)	Yield of methyl bromide[b] (%)
0.5	171	94.30
1.0	167	92.00
2.5	162	89.30
5.0	157	86.44
10.0	142	78.00
In situ	77	42.10

[a] 30% Excess over the theoretical requirement.
[b] Based on liquid bromine initially used.

In each set of the above experiments, the reaction was carried out in a 2-litre capacity glass reaction kettle having two necks of 29 B ground glass adapter in which a double walled reflux condenser and a 250 cm^3 capacity separating funnel were fitted. The mixture of methyl alcohol, water and sulphur was taken in the reaction kettle and heated to 348 K. A temperature of 348 K was maintained throughout the present study as it was found to be within the optimum range arrived at by the earlier workers.[12–15] The reactants were then gently mixed by means of a magnetic stirrer while adding liquid bromine. The unreacted methyl alcohol was returned to the reaction

Table 3. Effect of addition of water on the yield of methyl bromide (temperature of reaction, 348K; methyl alcohol, 120 cm^3; Liquid bromine [a], 50 cm^3; sulphur, 10.5 g)

Volume of water added (cm^3)	Excess over stoichiometric requirement[b] (%)	Weight of methyl bromide obtained (g)	Yield of methyl bromide[c] (%)
22.0	0.0	155	85.40
24.0	10.0	159	87.60
26.5	20.0	164	90.20
28.5	30.0	169	93.20
31.0	40.0	170	94.00
33.0	50.0	169	93.20

[a] Rate of addition was maintained at 0.5 cm^3 min^{-1}.
[b] Stoichiometric quantity of water is 22 cm^3 according to reaction (1).
[c] Based on liquid bromine initially used.

Table 4. Quantitative recovery of methyl bromide

Volume of liquid bromine (cm^3)	Volume of methyl alcohol (cm^3)	Weight of sulphur (g)	Volume of water (cm^3)	Weight of methyl bromide obtained (g)	Composition of methyl bromide obtained	(%)	Yield of methyl bromide (%)
350	840	73.5	200	1195	CH_3Br	97.90	93.80
					S_2Br_2	1.50	
					Br_2	0.50	
					H_2O	Traces	
525	1260	110	300	1802	CH_3Br	98.20	94.86
					S_2Br_2	1.00	
					Br_2	0.60	
					H_2O	Traces	
700	1680	147	400	2406	CH_3Br	97.60	94.60
					S_2Br_2	1.20	
					Br_2	0.70	
					H_2O	Traces	

mixture. The methyl bromide gas formed during the reaction was passed through a tower containing metallic copper turnings and soda lime granules to remove unreacted bromine and sulphur bromide. Subsequently the methyl bromide gas was passed through a fused calcium chloride tower to remove traces of moisture. The dry methyl bromide gas was collected in an evacuated glass chamber from which it was drawn intermittently, compressed and cooled for liquefaction. The methyl bromide was analysed by hydrolysis of a weighed quantity with monoethanolamine and estimating the bromide content by Volhard's method.[15]

3. Results and discussion

The conditions for the production of methyl bromide from methyl alcohol, sulphur, water and liquid bromine have been standardised. The data presented in Tables 1–4 support the theory put forward for the steps involved in the overall reaction viz., that the sulphur reduces bromine to sulphur bromide which in the presence of water forms hydrobromic and sulphuric acids. The reaction of optimum quantities of methyl alcohol, sulphur, water and liquid bromine, produced methyl bromide with an overall yield of 94.42% and a purity of 98.2%. A 5% increase in sulphur above the theoretical requirement improved the yield of methyl bromide from 80 to 85% which further raised to 94% in the presence of 30% excess of water that was required for the reaction.

The experiments carried out for total addition of liquid bromine in the initial stage gave very low yields, which was due to the formation and loss of gaseous sulphur bromide. An increase in the yield of methyl bromide with the rise in the quantity of excess water was due to the formation of hydrobromic and sulphuric acids by hydrolysis of sulphur bromide with water and prevented the loss of bromine in the form of gaseous sulphur bromide. It is known that sulphuric acid acts as a catalyst[16] in the formation of methyl bromide from hydrobromic acid and methyl alcohol. However in the present case sulphuric acid is a by-product of the reaction and it was found that sufficient quantity of sulphuric acid was formed to act as a catalyst and further addition did not increase the yield.

Since there is a wide difference in the rates of the overall reaction (1) and the initial reaction (2) it is necessary to carry out the initial reaction at a controlled rate for the maximum conversion of sulphur bromide to hydrobromic acid. Hence the reduction *in situ* of liquid bromine along with the reaction mixture of methyl alcohol, sulphur and water, gave a spontaneous evolution of gaseous sulphur bromide. A sufficient interval of time was required for sulphur bromide to react with water to form hydrobromic and sulphuric acids and hence liquid bromine was added at a slow rate over a period of 2–6 h to obtain maximum yield of methyl bromide with a minimum loss of both gaseous bromine and sulphur bromide.

Acknowledgements

The authors wish to express their sincere thanks to Dr B. L. Amla (Central Food Technological Research Institute, Mysore) for his keen interest and encouragement and also to Mr S. Younus Ahmed (Fermentation Technology Discipline) for his critical review of the experimental work.

References

1. Bridges, R. *J. Sci. Food Agric.* 1955, **6**, 261.
2. Winteringham, F. *J. Sci. Food. Agric.* 1955, **6**, 269.
3. German Patent 33 064, 1952.
4. Belgian Patent 507 922, 1952.
5. Indian Patent 124 893, 1971.
6. Indian Patent Cal/1270/75, 1977.
7. US Patent 2 244 629, 1941.
8. Steinkepf, W.; Schwen, G.; *J. Prakt. Chem.* 1921, **102**, 363.
9. Japan Patent 7 303 804, 1973.
10. British Patent 768 893, 1957.
11. US Patent 2 359 828, 1944.
12. British Patent 730 682, 1955.
13. Phillips, M. A. *Ind. Chemist*, 1963, **39**, 457.
14. German Patent (East) 14 892, 1958.
15. Vogel, A. I. *A Text-book of Quantitative Inorganic Analysis* The English Language Book Society and Longmans, London, 1968, 3rd edn. p. 267
16. Othmer K., *Encyclopedia of Chemical Technology* **3**, Interscience Publishers, John Wiley & Sons Inc., New York, USA, 1964, 2nd edn. p. 772.