Synthesis of lead dimethacrylate

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Synthesis of lead dimethacrylate from methacrylic acid and basic lead carbonate is discussed. A balanced chemical reaction is proposed and then justified by evaluating products of the reaction experimentally. Solubility characteristics of lead dimethacrylate are mentioned.

(Keywords: lead dimethacrylate; synthesis; methacrylic acid; lead carbonate; solubility)

INTRODUCTION

The family of methacrylic monomers is based on methacrylic acid (MAA), which is a simple α,β-unsaturated acid[1]. MAA offers two types of chemical reactions. One is polymerization, involving the double bond and other condensation, involving the carboxylic acid group. The reactions involving the carboxylic acid group are characteristic of an organic acid and yield anhydrides, esters, nitriles and salts[2]. Salts of MAA that have been reported so far are: zinc, magnesium, barium, nickel, strontium and mercury[3]. A simple method of synthesizing lead salt of MAA is reported in this paper.

EXPERIMENTAL

Materials

MAA and basic lead carbonate (BLC) of pure grade were used in all the reactions. Specifications of both the chemicals are given in *Table 1*. MAA was obtained from Polymers Corporation of Gujarat Limited, Baroda (India).

Table 1 Properties of methacrylic acid (MAA) and basic lead carbonate (BLC)

Property	MAA	BLC
Physical state	Clear liquid	White powder
Formula	$C_4H_6O_2$	$C_2H_2O_8Pb_3$
Structure	$CH_2=C(CH_3)COOH$	$(PbCO_3)_2 \cdot Pb(OH)_2$
Molecular weight	86.06	775.60
Freezing point (°C atm)	15	—
Boiling point (°C atm)	160	400 (dec.)
Specific gravity	1.015	6.14
Water content (%)	0.22	Nil
Inhibitor (ppm)	250 MEHQ	Nil

Chemical reaction

The possible reaction between MAA and BLC may be expressed in two steps:

$$(PbCO_3)_2 + 4\,MAA \rightarrow 2\,LDM + 2CO_2 + 2H_2O \quad (1)$$

$$Pb(OH)_2 + 2\,MAA \rightarrow LDM + 2H_2O \quad (2)$$

The overall reaction may be summarized as:

$$BLC + 6\,MAA \rightarrow 3\,LDM + 2CO_2 + 4H_2O \quad (3)$$

Thus, the reaction between 1 mol BLC and 6 mol MAA can produce 3 mol lead dimethacrylate (LDM), 2 mol carbon dioxide and 4 mol water. The structure of LDM may be considered as:

$$CH_2=C(CH_3)-OCO-Pb-OCO-(CH_3)C=CH_2 \quad (4)$$
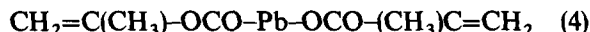
Equation (3) is a balanced reaction and its theoretical justification may be given by stochiometric considerations (*Table 2*).

Method

A 250 ml-capacity round bottom flask with a Teflon-covered magnetic bar was weighed accurately. The flask was then charged with 1 mol (0.04 g mol wt) of MAA and 0.1 mol (0.004 g mol wt) of BLC. The flask was attached to a condensor and the mixture was stirred adequately with a magnetic stirrer. The reaction was maintained at 30°C and agitation continued till the white powder of BLC disappeared in MAA to form a clear solution. The completion of reaction was ensured by stirring the mixture for an additional 10 min. The flask was removed

Table 2 Stochiometric consideration of equation (3)

	Components	Mol	Molecular weight	Gram molecular weight	Total
Reactants	BLC	1	775.60	775.60	1291.96
	MAA	6	86.06	516.36	
Products	LDM	3	377.28	1131.84	1291.94
	CO_2	2	44.01	88.02	
	H_2O	4	18.02	72.08	

from the condensor and was weighed along with reaction mixture and the bar.

The reaction mixture was analysed for water content by the Karl–Fischer method. All samples were weighed to an accuracy of 0.1 mg. The amount of carbon dioxide produced was calculated as weight difference of mixture before and after reaction.

This experiment was repeated using a fixed quantity of MAA and variable quantity of BLC ranging from 0.1 to 0.5 mol. Results are given in *Table 3*.

Viscosity of the reaction mixture was found to increase with the increasing amount of BLC used in the reaction. Sufficient agitation was maintained by increasing the speed of the magnetic stirrer.

BLC powder, especially beyond 0.4 M concentration, was added gradually to avoid excessive thickening of the reaction mixture. Moreover, at higher BLC concentrations, the reaction was found to take a long time thereby indicating a decrease in the reaction rate. This deficiency was overcome by increasing the temperature to 40°C.

An important matter relating to temperature is the inhibition of MAA to avoid premature polymerization. The reaction at 30°C could successfully be carried out used MAA with 250 ppm monomethylether of hydroquinone (MEHQ). However, while carrying out the reaction at elevated temperature, the inhibitor level was increased to 500 ppm. The increase in reaction temperature was restricted to prevent the facilitation of undue polymerization. It is believed that MEHQ inhibits MAA as well as LDM in the reaction mixture.

RESULTS AND DISCUSSION

The reaction of MAA and BLC generates simple molecules of water (liquid) and carbon dioxide (gas). Amounts of these products with respect to various mole proportions of the reactants can be calculated from equation (3). Calculated quantities are expressed as theoretical values in *Table 3*. Experimentally determined values are expressed as practical values. It is evident from *Table 3* that theoretical and practical values of water and carbon dioxide are in good agreement, thereby justifying the validity of equation (3).

The common observation that viscosity increases with progress of the reaction is probably due to the formation of LDM which is a relatively bigger molecule possessing bulky methyl groups.

After 0.5 M addition of BLC, the reaction mixture was stored at 25°–30°C for 24 h. Translucent crystals were formed in the mixture. The liquid was separated by decantation and a portion of the crystals was washed with water to remove unreacted MAA. The crystals were dried

under vacuum and stored away from any direct source of light and heat.

A known quantity of crystals was dissolved in MAA at 50°C and was reacted with sufficient quantity of 5% aqueous sulphuric acid which gave a white precipitate of lead sulphate. This result indicated a route to determine gravimetrically the lead content of LDM through lead sulphate. The amount of lead was 54.64 mol% LDM which is in accordance with the corresponding theoretical value of 54.92 mol%. This assessment provides an alternative conformation of formation of LDM as per the formula[4].

The crystals of LDM melts at 70°C and the liquid remains stable at higher temperatures. The stability may be attributed to the presence of lead in the molecule. Solubility characteristics of LDM with respect to various common solvents are shown in *Table 4*.

LDM is a monomer and may find application as a cross-linking agent and also as a material to provide radiation shielding properties.

NOTE

BLC possesses adequate basicity against acidic nature of MAA and that is why the reaction becomes effective even at room temperature.

During the reaction, effervescence of carbon dioxide gas was observed indicating the progress in the reaction. The effeverscence was observed to a lesser extent because BLC is partly a carbonate and partly a hydroxide. With higher viscosity of the mixture effervescence decreases. In this situation, it is suggested that the reaction mixture may be subjected to a partial vacuum periodically to remove occluded carbon dioxide.

MAA is consumed progressively in the reaction and,

Table 4 Qualitative assessment of solubility characteristics of LDM

Solvent/Monomer	Solubility at	
	30° C	60° C
Water	I	I
Acetone	S	S
Methanol	S	S
Benzene	SS	S
Petroleum ether (80–100)	I	SS
Carbon tetrachloride	I	SS
Chloroform	SS	S
Styrene	I	SS
Methyl methacrylate	S	S
Methacrylic acid	SS	S

I = insoluble
S = soluble
SS = sparingly soluble

Table 3 Analytical data of reaction products

Reaction no.	Mole proportion of MAA	Mol proportion of BLC	Per cent water		Per cent carbon dioxide	
			A	B	A	B
1	1	0.1	1.231	1.215	1.48	1.38
2	1	0.2	2.199	2.179	2.62	2.38
3	1	0.3	2.988	2.945	2.53	3.38
4	1	0.4	3.640	3.607	4.26	4.17
5	1	0.5	4.186	4.133	4.87	4.77

A = Theoretical values
B = Practical values

therefore, the amount of MAA remaining unreacted at a particular time interval may be taken as a criterion of reaction progress. However, as BLC is essentially basic, a decrease in acidity cannot be strictly attributed to acid consumption in the reaction.

ACKNOWLEDGEMENT

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