

VINYL MONOMER COMPLEXES

Part II. The complexes of methyl methacrylate
and Methylacrylate with Zinc Chloride and Platinic Chloride

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Complexes of methyl methacrylate and of methyl acrylate with $ZnCl_2$ and $H_2 PtCl_6$ were prepared. methyl methacrylate and methylacrylate from complexes ($MMA \rightarrow Mx_n$, $MA \rightarrow Mx_n$) with inorganic salt through carbonyl group in the 1:1 (monomer:salt) molar ratio. These complexes are hygroscopic and soluble in acetone and chloroform. The possible structures of the complexes are also proposed.

INTRODUCTION

In the preceding paper (1) it was reported that acrylonitrile forms complexes with some inorganic salts like $CuCl_2$, $CoCl_2$, $HgCl_2$, $ZnCl_2$, $PtCl_6$ and $CrCl_3$. The complexation takes place through the nitrile group in the 1:1 (AN:salt) molar ratio resulting in delocalization of the electrons in the double bond of the complexed monomers. The complexes of acrylonitrile with the above mentioned salts undergo polymerization easier than the uncomplexed monomers. The accelerating or inhibiting effects of these complexes upon the copolymerization of acrylonitrile with styrene and acrylonitrile with allyl alcohol were also observed (2-5).

This paper deals with the preparation of the complexes of methyl-methacrylate and methylacrylate with zinc chloride and platinic chloride.

EXPERIMENTAL

Materials

1. Methyl methacrylate (BDH) was first washed with sodium hydroxide to remove the inhibitor present in the monomer and then with water and dried over anhydrous calcium chloride. It was then distilled at 99° .

2. Methyl acrylate (BDH) was first washed several times with NaOH to remove the inhibitor and then with water. Finally it was dried over calcium sulphate. The monomer was distilled at 80.5°

3. Laboratory grade methanol, acetone and chloroform were purified according to known methods.

4. Extra pure anhydrous zinc chloride ($ZnCl_2$) of E., Merck and laboratory reagent grade chloroplatinic acid ($H_2 PtCl_6 \cdot H_{20}$) of BDH were used without further purification.

Procedure for Preparation of Complexes (6).

1. *Complexes of methyl methacrylate with zinc chloride and platinic chloride:* A known amount of each inorganic salt was dissolved in excess methyl methacrylate by heating at 50° for 30 min. Excess methyl-methacrylate was then distilled off at room temperature under reduced pressure. The resulting complex was kept for 5 hr. in a vacuum desiccator. The composition of the complexes was determined from the weight of the salt initially used and of the resulting complex. The results are given in Table 1. These results indicate that methylmethacrylate forms complexes with zinc chloride and platinic chloride in 1:1.077 and 1:0.989 (MMA:salt) molar ratio respectively. The IR spectra of the complexes were also recorded.

2. *Complexes of methyl acrylate with zinc chloride and platinic chloride:* A known amount of each salt was added to a ground neck tube already containing methyl acrylate in excess. The salt was dissolved in the monomer by heating at 50° for 30 min. Excess of methyl acrylate was distilled off under reduced pressure. The resulting complex was further kept in a vacuum desiccator for 5 hr. The composition of the complexes were determined from the weight of each salt initially taken and of the resulting product. The results are shown in Table 2. These results indicate that methyl acrylate forms complexes with platinic chloride and zinc chloride in 1:0.74 and 1:0.962 (MA:salt) molar ratio respectively. IR spectra of the complexes were also recorded.

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Table 1: The composition of complexes of methyl methacrylate (MMA) with zinc chloride and platinum chloride

Salt	Amount of salt (moles)	Amount of MMA consumed (moles)	Composition of complex (MMA/M _{x_n}) mole ratio.	IR spectrum wave number	Physical properties
1. ZnCl ₂	3.669 x 10 ⁻⁴	3.953 x 10 ⁻⁴	1.077	C = O 1740 cm ⁻¹ -CH=CH ₂ 1450 cm ⁻¹	Highly hygroscopic, colourless substance, soluble in acetone and chloroform.
2. H ₂ .PtCl ₂ .H ₂ O	1.169 x 10 ⁻⁴	1.56 x 10 ⁻⁴	0.989	C = O 1940 cm ⁻¹ -CH=CH ₂ 1180 cm ⁻¹	Highly hygroscopic, dark brownish substance, soluble in acetone and chloroform.

Table 2: The composition of complexes of methyl acrylate (MA) with zinc chloride and platinum chloride

salt	Amount of salt (moles)	Amount of MA consumed (moles)	Composition of complex (MA/M _{x_n}) Mole ratio	IR spectrum	Physical properties
1. ZnCl ₂	3.669 x 10 ⁻⁴	3.529 x 10 ⁻⁴	0.962	C = O 1725 cm ⁻¹ -CH=CH ₂ 1420 cm ⁻¹	Hygroscopic, colourless substance, soluble in acetone and chloroform.
2. H ₂ PtCl ₆ .H ₂ O	1.683 x 10 ⁻⁴	1.639 x 10 ⁻⁴	0.974	C = O 1710 cm ⁻¹ -CH=CH ₂ 1490cm ⁻¹	Hygroscopic, dark brown substance soluble in acetone and chloroform

RESULTS AND DISCUSSION

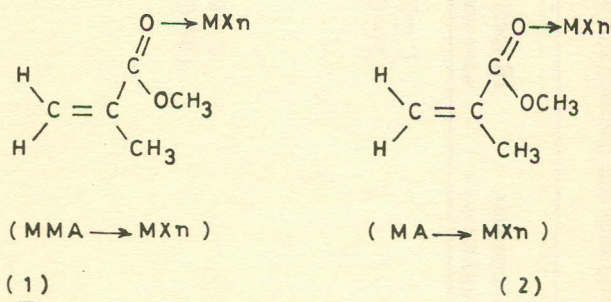
The results obtained from the preparation of complexes of methyl methacrylate and methylacrylate with zinc chloride and platinum chloride are summarized in Table 1 and 2.

The results given in Table 1 show that zinc chloride and platinum chloride both form complexes in 1:1 (MMA:salt) molar ratio. The MMA.ZnCl₂ complex was colourless, viscous and hygroscopic liquid soluble in acetone and chloroform, whereas the MMA.PtCl₆ complex was a brown hygroscopic substance soluble in chloroform and acetone. The spectrum of MMA.ZnCl₂ complex shows a carbonyl band at 1740 cm⁻¹ and a vinyl band at 1450 cm⁻¹ frequency, whereas the MMA.PtCl₆ complex shows a carbonyl absorption band at 1940 cm⁻¹ frequency and a vinyl band at 1480 cm⁻¹ frequency. The carbonyl band of the monomer itself is at 1650 cm⁻¹ frequency and the vinyl band at 1440 cm⁻¹ frequency.

The results summarized in Table 2 show that ZnCl₂ and PtCl₆ form complexes in the 1:1 (MA:salt) molar ratio. These complexes are found hygroscopic and soluble in acetone and chloroform. The spectrum of MA.ZnCl₂ complex show carbonyl (C=O) absorption band at 1725 cm⁻¹ frequency and vinyl band at 1420 cm⁻¹ frequency whereas the MA.PtCl₆ complex shows a carbonyl band at 1710 cm⁻¹ frequency and a vinyl band at 1490 cm⁻¹. The carbonyl group of the monomer itself is at 1650 cm⁻¹ and vinyl band at 1440 cm⁻¹ frequency.

The I R spectral studies of the complexes of methyl methacrylate and methyl acrylate with ZnCl₂ and PtCl₆ show the shift of carbonyl absorption band from lower to higher wave number as compared with the spectra of monomers. The shift of the carbonyl absorption band towards longer frequency suggests that complexation takes place through carbonyl group of the monomers [6, 7]. In earlier studies several workers [6,8] have prepared the complex of zinc chloride with MMA. The MMA.ZnCl₂ complex was a colourless, viscous, hygroscopic liquid with the composition of 1:1 (MM:salt) molar ratio. The infra-red spectra showed the shift of carbonyl absorption band to a longer wave number compared with the absorption band of MMA showing the complexation through carbonyl group. In an earlier paper (1) these authors have already imported the preparation of the complexes of acrylonitrile with some inorganic salts like CuCl₂, CoCl₂, HgCl₂, ZnCl₂, PtCl₆ and CrCl₃. I R spectral studies showed that the shift of the nitrile absorption band from lower to higher frequency suggested that the complexation takes place through the nitrile group.

In the presence of inorganic salt, MMA or MA form complexes with zinc chloride and platinum chloride through the carbonyl group (C=O) due to the delocalization of π-electrons in the double bond of the complexed monomers. Due to formation of complexes, MMA and MA with ZnCl₂ and PtCl₆, the polarity of the monomer may be increased and the electron accepting character of complexed monomers as compared with uncomplexed monomers also get enhanced [2-6]. However the complexation of vinyl monomers with certain inorganic salts results increased reactivity of these monomers in homo and copolymerization [9-11]. The proposed structure of the complexes may be as follows:



MX_n = metal salt

REFERENCES

1. S.A.K. Lodhi and A. Rasheed Khan, *Revue Roum. de chimie*, **27**, 509 (1982).
2. S.A.K. Lodhi and A. Rasheed Khan, *Revue Roum de chimie* (in press), 1983.
3. Shigeru Yabumoto, K. Ishi and K. Arita, *J. Polymer Sci., Part A-1* **7**, 1577 (1969).
4. S.A.K. Lodhi and A. Rasheed Khan, *J. Chem. Soc. Pakistan* **4**, 129 (1982).
5. S.A.K. Lodhi and A. Rasheed Khan, *Pakistan J. Sci. Ind. Res.* **26**, 3, 162 (1983).
6. M. Imoto, T. Otsu and Y. Harada, *Makromole. Chem.*, **65**, 180 (1983).
7. H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).
8. W. Kuran, S. Pasynkiewicz, Z. Florjanczyk and E. Luszyk, *Makromole Chem.* **177**, 2627 (1976).
9. J. Furukawa, E. Kobayashi, S. Nagata and T. Moritani, *J. Polymer Sci., Polymer Chem Ed.* **12**, 1799 (1974).
10. N. G. Gaylord and A. Takahashi, *J. Polymer Sci. Letters*, **6**, 743 (1968).
11. N. G. Gaylord and A. Takahashi, *J. Polymer. Sci. Letters* **6**, 749 (1968).