

A study on reaction between chloroformaldehyde and potassium permanganate

Author: Abhijit Mallick

Department of Chemistry, Academy of Technology

P.O. AEDCONAGAR, Adisaptagram, Dist. Hooghly 712121, W.B. India.

Abstract

The earlier study of the author shows that chloroform reacts with nitric acid to form chloroformaldehyde. The objective of the present study is to investigate the nature of chemical reaction between chloroformaldehyde and acidified potassium permanganate solution. Aldehydes are oxidized to form corresponding carboxylic acids in presence of oxidizing agent like acidified potassium permanganate solution. Chloroformaldehyde is also oxidized by acidified potassium permanganate solution but unlike other aldehydes oxidation of chloroformaldehyde produces only carbonic acid instead of any carboxylic acid.

Detailed investigation clearly indicates that chloride ion is formed during the chemical reaction between chloroformaldehyde and potassium permanganate. Furthermore, the reaction product mixture does not respond ferric chloride test for formic acid. Even the product does not respond alkaline $KMnO_4$ solution test for formic acid.

On the basis of experimental studies, a probable mechanism is proposed to explain the reaction between chloroformaldehyde and potassium permanganate. The mechanism shows that only carbonic acid is formed during the reaction between chloroformaldehyde and potassium permanganate.

Keywords Chloroformaldehyde, Potassium permanganate, Silver nitrate, Ferric chloride, Carbonic acid.

Introduction

Properties and applications of chloroform are well documented in the literature¹⁻⁴. Thermo-chemical properties of chloroform have been developed and documented by Chase M.W. Jr.⁵. Barta, Kooner, et al.⁶ studied details of thermodynamics of complex formation in chloroform and other organic compounds. Similar studies on complex formation in chloroform-dimethyl sulphoxide mixture are also documented⁷. Al'per, Peshekhodov, et al.⁸ studied details of intermolecular interactions on chloroform-acetone system. It has been reported⁹ that aldehydes are oxidized by acidified potassium permanganate solution to corresponding carboxylic acids. The study of Mallick¹⁰ shows that nitric acid treatment on chloroform gives rise to chloroformaldehyde. Mallick¹¹ also showed that chloroformaldehyde on reaction with benzoyl peroxide produces chlorobenzyl formate.

The present paper deals with a detailed study of the reaction between chloroformaldehyde and acidified potassium permanganate solution at room temperature. The detailed study shows that formic acid is not formed during oxidation of chloroformaldehyde by acidified potassium permanganate solution. So, like other aldehydes, chloroformaldehyde is not converted to corresponding carboxylic acid on treatment with acidified potassium permanganate solution. The proposed mechanism suggests that one molecule potassium permanganate consumes two molecules chloroformaldehyde forming carbonic acid and $MnCl_2$.

Material and Methods

1. Preparation of 1: 1 nitric acid 50 ml double distilled water is taken in a 250 ml beaker. 50 ml laboratory grade concentrated nitric acid is added slowly to it. So 100 ml 1:1 nitric acid is prepared.

2. Following reagents are used

- (a) $AgNO_3$ solution of strength (N/50), (b) NH_4OH solution of strength 1(N),
(c) $KMnO_4$ solution of strength (N/20), (d) $NaHCO_3$ solution of strength 1(N),
(d) 1% $FeCl_3$ solution.

3. 40 ml laboratory grade chloroform is taken in a reflux apparatus. 20 ml 1: 1 nitric acid is added to it. The mixture is heated to about 90°C for 45 min under reflux. The heater is put off and the mixture is then allowed to cool to room temperature under reflux. The heterogeneous mixture is collected and kept in a refrigerator for 1 hr. Two layers, organic and aqueous, are quite distinct. The heavier organic layer forms the bottom layer and lighter aqueous layer forms the top layer. These two layers are separated by using a separating funnel. Both the bottom layer and aqueous layer are believed to contain chloroformaldehyde¹⁰. Litmus paper test shows that both the layers are acidic.

4. 4 ml aqueous layer is taken in a 250 ml conical flask. 1 ml freshly prepared (N/20) $KMnO_4$ solution is added into it. Shake the mixture slowly. The purple colour of $KMnO_4$ vanishes. $KMnO_4$ solution is added with shaking by 0.5 ml continuously till very light pink colour persists. The flask is stoppered and kept in dark for 8 hrs. After that the flask is taken out. Nearly colourless solution is obtained. So the $KMnO_4$ -treated-aqueous-layer is prepared. Similar way $KMnO_4$ - treated-organic-layer is also prepared.

5. 3 ml $KMnO_4$ -treated-aqueous-layer is taken in a 250 ml conical flask. 5 ml distilled water is added into the flask. Freshly prepared 2 ml (N/50) silver nitrate solution is added to it. A white precipitate is obtained and the precipitate is readily dissolved by adding freshly prepared 1(N) ammonium hydroxide solution drop-wise. Same observation is noticed when 2 ml (N/50) silver nitrate solution is added to 3 ml $KMnO_4$ -treated-organic-layer followed by ammonium hydroxide solution as described above.

6. 3 ml $KMnO_4$ -treated-aqueous-layer is taken in a 250 ml conical flask. The solution is made alkaline by adding freshly prepared 1(N) $NaHCO_3$ solution drop-wise. Red litmus paper is used for this purpose. Then 4 drops of freshly prepared (N/20) $KMnO_4$ solution is added into it. The solution is purple in colour. Shake the mixture slowly. The flask is stoppered and kept in dark for half-an-hour. The purple colour of $KMnO_4$ persists. The same observation is noticed when 4 drops of freshly prepared (N/20) $KMnO_4$ solution is added into alkaline $KMnO_4$ -treated-organic-layer.

7. In one set of experiment 3 ml $KMnO_4$ -treated-aqueous layer is taken in a 250 ml conical flask. Add 1 drop of phenolphthalein indicator. The solution remains colourless. Add 5 drops of freshly prepared 1% $FeCl_3$ solution with shaking. The solution appears yellow in colour due to the presence of $FeCl_3$. The conical flask is stoppered and kept in dark for 30 minutes. Yellow colour of $FeCl_3$ persists in the solution.

In another set of experiment 3 ml $KMnO_4$ -treated-aqueous-layer is taken in a 250 ml conical flask. The solution is made alkaline by adding freshly prepared 1(N) NH_4OH solution drop-wise with shaking. Red litmus paper is used for this purpose. The mixture is slightly warmed to ward off excess ammonia. Cool the mixture to room temperature. Then add 5 drops of freshly prepared 1% $FeCl_3$ solution with shaking. The solution appears yellow in colour due to the presence of $FeCl_3$. The conical flask is stoppered and kept in dark for 30 minutes. The solution remains yellow in colour. No characteristic red solution of ferric formate is observed.

Both sets of experiments are carried out using 3 ml $KMnO_4$ -treated-organic-layer also. Same observation is noticed.

8. NMR study of the $KMnO_4$ -treated-aqueous-layer is conducted by JEOL 400 MHz NMR spectrophotometer.

Results and Discussion

1. Both aqueous layer and organic layer are treated with (N/20) $KMnO_4$ solution separately. $AgNO_3$ test was carried out in both $KMnO_4$ -treated-aqueous-layer and $KMnO_4$ -treated-organic-layer separately. The observation suggests that chloride ion (Cl^-) be formed during the reaction between chloroformaldehyde and $KMnO_4$.

2. It is known that formic acid reduces alkaline $KMnO_4$ solution, producing brown precipitate of MnO_2 . The present study shows that on drop-wise addition of $KMnO_4$ in both alkaline $KMnO_4$ -treated-aqueous-layer and alkaline $KMnO_4$ -treated-organic-layer samples, purple colour of $KMnO_4$ persists without any precipitation of MnO_2 . The observation indicates that formic acid may be absent in both $KMnO_4$ -treated-aqueous-layer and $KMnO_4$ -treated-organic-layer.

3. It is believed that yellow colour of $FeCl_3$ solution becomes colourless in presence of formic acid due to the formation of soluble ferric formic acid complex. Furthermore, in presence of ammoniacal $FeCl_3$ solution, formic acid forms characteristic red coloured complex with ferric ion. In the present study, on drop-wise addition of $FeCl_3$ solution in both $KMnO_4$ -treated-aqueous-layer and $KMnO_4$ -treated-organic-layer, yellow colour of $FeCl_3$ solution remains unchanged even under ammoniacal condition. The observation suggests that formic acid be not formed during acidified $KMnO_4$ treatment on chloroformaldehyde.

4. The Fig.1 shows the NMR spectrum of $KMnO_4$ -treated-aqueous-layer sample.

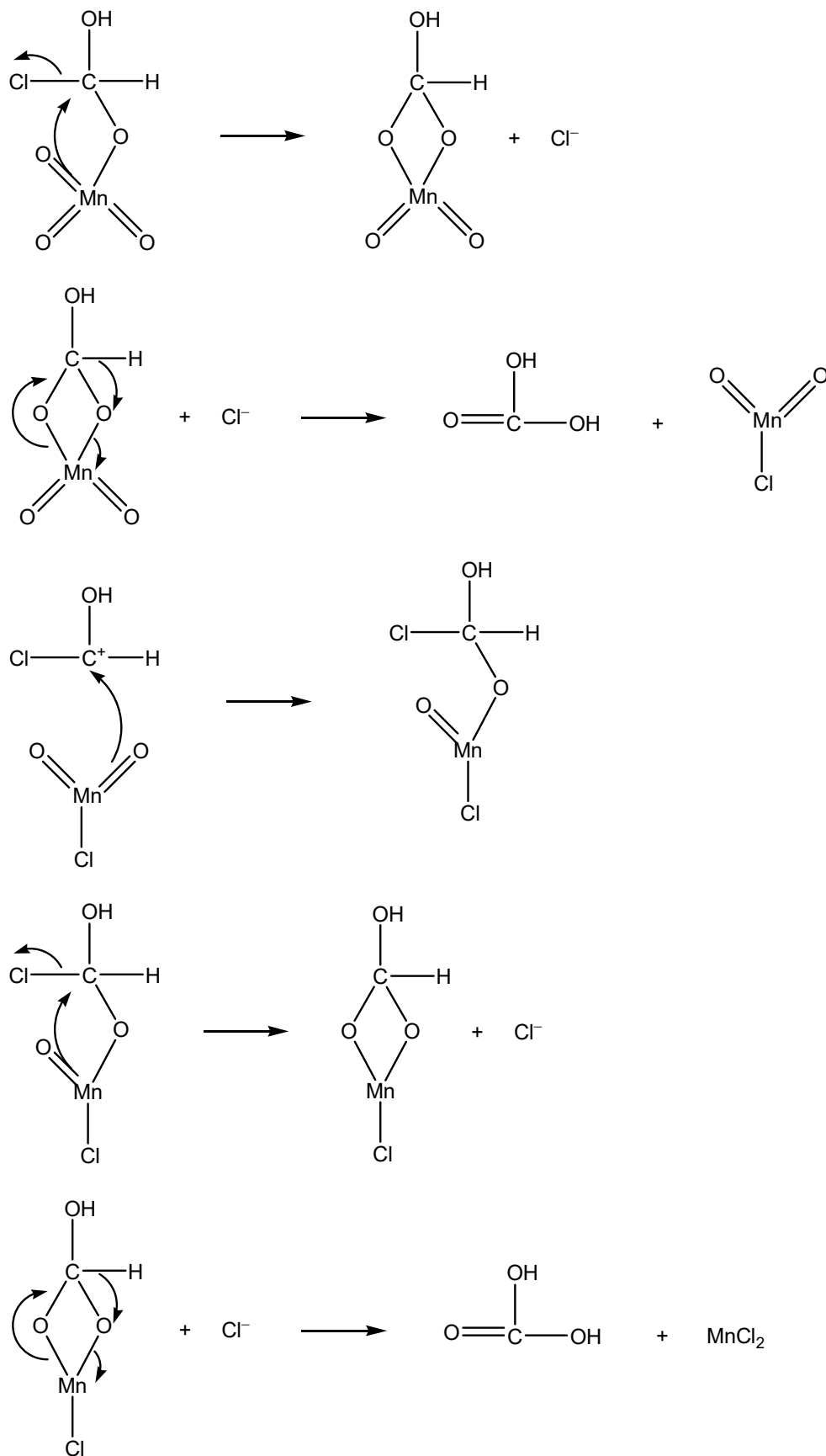


Figure.2 Proposed mechanism of the reaction between chromoformaldehyde and acidified $KMnO_4$.

Conclusion

Chloroformaldehyde is oxidised by acidified $KMnO_4$ solution but unlike other aldehydes, it produces only carbonic acid instead of formic acid.

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