

## A study on reaction between chloroform aldehyde and acidified potassium iodide solution

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### 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 potassium iodide. It is a redox reaction where chloroformaldehyde oxidizes iodide ion in presence of acid to iodine and itself gets converted to 1,2-dichloro glycol. The reaction continues till chloroformaldehyde is available in the mixture. Preliminary studies show that the reaction is slow but it continues steadily as iodine is removed from the mixture. As reaction proceeds, chloroform gets converted to chloroformaldehyde, which ultimately results single aqueous phase. Detailed investigation clearly indicates that iodine is formed during the reaction between chloroformaldehyde and potassium iodide in presence of acid. Furthermore, the product mixture shows positive response to ammonium ceric nitrate test for alcoholic group. The NMR spectrum of the product sample shows a single broad peak presumably due to merging of two peaks. On the basis of experimental studies, a mechanism is proposed to explain the reaction between chloroformaldehyde and potassium iodide. The mechanism shows that iodide ion is oxidized to iodine and chloroformaldehyde is reduced to alcohol, which finally dimerises to 1,2-dichloro glycol.

**Keywords:** Chloroformaldehyde, Potassium iodide, Dimerization, 1,2-Dichloroglycol, Iodine, Sodium thiosulphate.

### Introduction

Properties and applications of chloroform are well documented in the literature<sup>1-4</sup>. Thermo-chemical properties of chloroform have been developed and documented by Chase M.W. Jr.<sup>5</sup>. Barta, Kooner, et al.<sup>6</sup> 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 documented<sup>7</sup>. Al'per, Peshekhodov, et al.<sup>8</sup> studied details of intermolecular interactions on chloroform-acetone system. It has been reported<sup>9</sup> that aldehydes are oxidized by acidified potassium permanganate solution to corresponding carboxylic acids. The study of Mallick<sup>10</sup> shows that nitric acid treatment on chloroform gives rise to chloroformaldehyde. Mallick<sup>11</sup> also showed that chloroformaldehyde on reaction with benzoyl peroxide produces chlorobenzylformate.

The present paper deals with a detailed study of the reaction between chloroformaldehyde and acidified potassium iodide solution at room temperature. The detailed study shows that chloroformaldehyde acts as oxidizing agent in acidic medium. Iodide ion acts as reducing agent and is oxidized to iodine. The proposed mechanism suggests that chloroformaldehyde be first converted to chloro-iodo-methanol in presence of acidified potassium iodide solution. Finally the alcohol dimerises to glycol with the release of iodine.

### 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) Laboratory grade Chloroform,                      (b) Freshly prepared KI solution of strength (N/10),

- (c) Freshly prepared  $Na_2S_2O_3$  solution of strength ( $N/10$ ),  
(d) Freshly prepared ammonium ceric nitrate solution (1%).

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  $90^\circ\text{C}$  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 chloroformaldehyde<sup>10</sup>. Litmus paper test shows that both the layers are acidic.

4. Exact 4 ml organic layer, containing chloroformaldehyde, is taken in a 250 ml conical flask. 10 ml distilled water is added into it. Few drops of (1:1)  $HNO_3$  is added into it. So the heterogeneous mixture is prepared. 1 ml ( $\frac{N}{10}$ ) KI solution is added into it. Shake the mixture slowly. The conical flask is stoppered and kept in refrigerator for 4 hours. The organic layer turns purple colour and the aqueous layer turns deep brown colour. The conical flask is taken out and the solution is titrated against ( $\frac{N}{10}$ )  $Na_2S_2O_3$  solution till the solution turns colourless. The conical flask is again stoppered and kept in refrigerator for 24 hours.

5. After 24 hours the conical flask is taken out. The organic phase of the mixture appears purple and the aqueous phase appears dark brown. The mixture is then titrated against ( $\frac{N}{10}$ )  $Na_2S_2O_3$  solution till the whole mixture turns colourless. The conical flask is again stoppered and kept in refrigerator for 24 hours.

6. The step 5 is repeated thrice for every 24 hrs. The organic layer disappears. The mixture appears homogeneous and brown colour. It is then again titrated against ( $\frac{N}{10}$ )  $Na_2S_2O_3$  solution till the homogeneous mixture turns colourless. The conical flask is again stoppered and kept in refrigerator for 24 hours.

7. After 24 hours the conical flask is taken out. The homogeneous solution remains colourless. So KI treated chloroformaldehyde solution is prepared. Herein after this homogeneous solution is called **sample**. Total volume of ( $\frac{N}{10}$ )  $Na_2S_2O_3$  solution consumed during this process is 4.1 ml.

8. Around 2 ml of sample, prepared in step 7, is taken in a 100 ml beaker. 5 ml distilled water is added into it. Freshly prepared ammonium ceric nitrate solution (1%) is added slowly into the beaker. The solution turns red, indicating the presence of alcoholic  $-OH$  group in the sample.

9. NMR study of the sample is conducted by JEOL 400 MHz NMR spectrophotometer.

## Results and Discussion

1. The reaction between chloroformaldehyde and acidified KI solution shows that iodine is liberated due to which organic layer appears purple and aqueous layer appears deep brown.

Iodine is initially neutralized by sodium thiosulphate solution so that the heterogeneous mixture turns colourless but iodine is regenerated after some time and the heterogeneous mixture again appears coloured. This observation suggests that the reaction between chloroformaldehyde and acidified KI solution be slow. However, the reaction is accelerated as iodine is removed by sodium thiosulphate solution.

2. The sample gives positive response to ammonium ceric nitrate test of alcoholic  $-OH$  group.

3. The HNMR spectrum of the sample is shown below

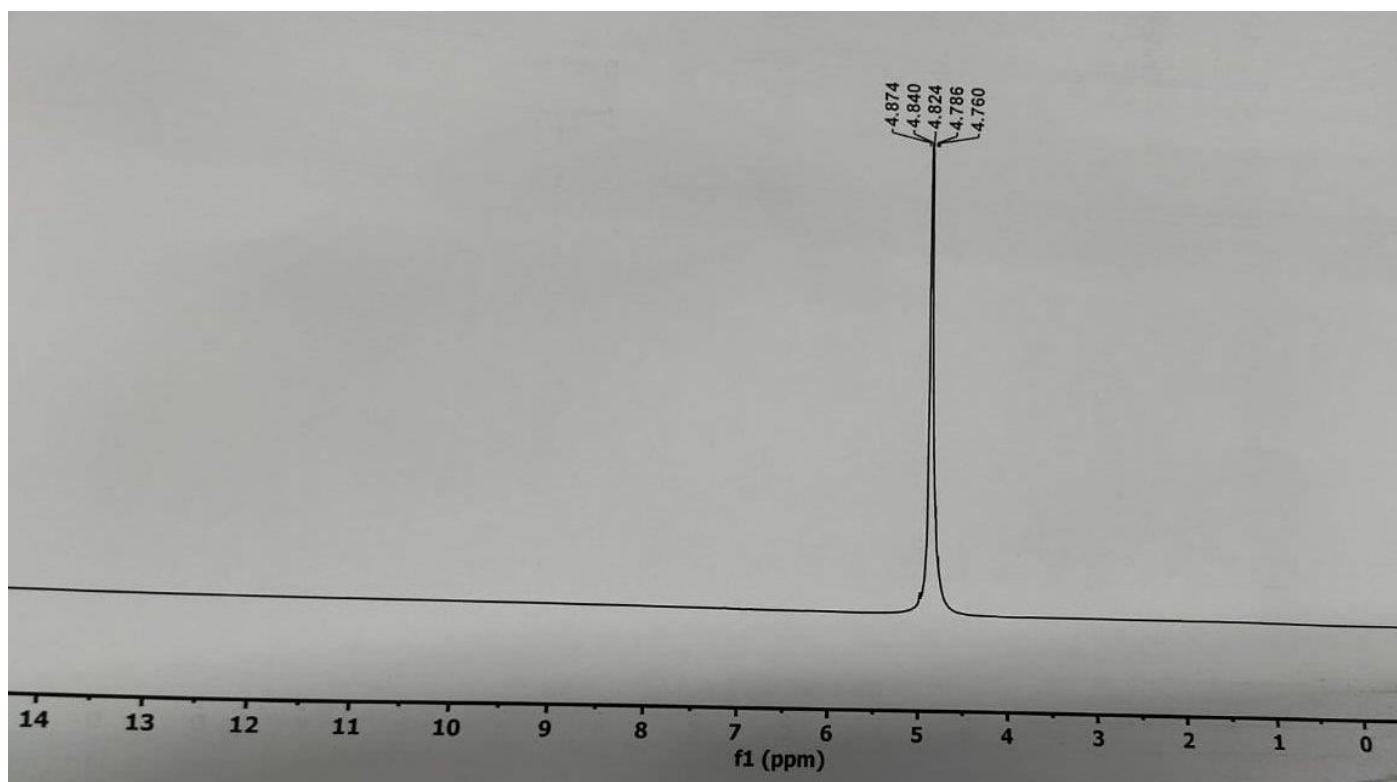
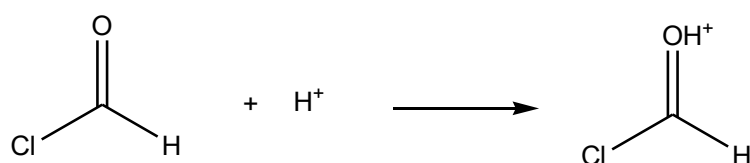


Figure 1: HNMR spectrum of the sample.

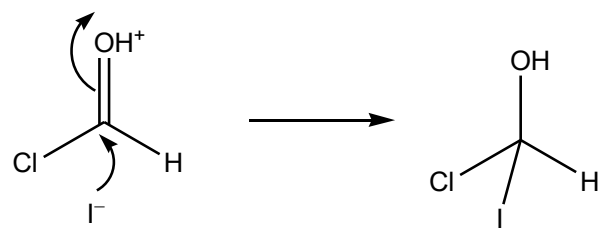
The spectrum shows only one broad peak at around 4.8 ppm. The peak height indicates that more than one  $-OH$  group may be present in the sample molecule. No peak is observed for chloroform and  $-CHO$  group although the experiment has been started with organic layer of nitric acid treated chloroform. Two different proton signals  $H^a$  and  $H^b$  (Figure 2) are expected. It is believed that strong  $-I$  effect of  $-Cl$  group causes downfield shifting for both the signals such that the two peaks are very close to merge into a broad peak.

4. On the basis of above observations the following mechanism is proposed. Acidified  $KI$  solution acts as reducing agent. It is believed that iodide ion acts as nucleophile to react with the  $-CHO$  group to form chloro-iodo-methanol as intermediate. The intermediate finally dimerises to 1,2-dichloro glycol and iodine is produced as byproduct. This iodine reacts with  $Na_2S_2O_3$  to form iodide ion, which again reacts with chloroformaldehyde to regenerate iodine. The reaction is continued till chloroformaldehyde is available in the aqueous phase of the heterogeneous mixture. Then chloroformaldehyde diffuses from organic layer to aqueous layer and the reaction continues but concentration of chloroformaldehyde in organic layer decreases. To maintain chloroformaldehyde concentration in the organic layer, chloroform reacts with nitric acid, present in the mixture and slowly gets transformed to chloromormaldehyde. Eventually all chloroform is transformed to chloroformaldehyde, producing a homogeneous aqueous solution.

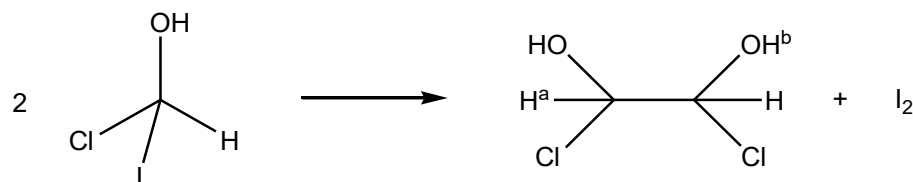
Step-1



Step-2



Step-3



Step-4



$I^-$  then again reacts with chloroformaldehyde (Step-2)

**Figure 2: Proposed mechanism illustrating conversion of chloroformaldehyde to 1,2-dichloro ethylene glycol.**

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