A STUDY ON REACTION BETWEEN CHLOROFORMALDEHYDE AND SODIUM HYDROXIDE

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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 sodium hydroxide solution. Aldehydes with no α − H atom follow Cannizzaro reaction with sodium hydroxide to form corresponding acid and alcohol. Chloroformaldehyde also does not have any α − H atom, but it does not follow Cannizzaro reaction, producing only formic acid on reaction with sodium hydroxide. Detailed investigation clearly indicates that chloride ion is formed during the chemical reaction between chloroformaldehyde and sodium hydroxide. Furthermore, the reaction product mixture does not respond to ceric ammonium nitrate test of alcohol group. On the basis of experimental studies, a probable mechanism is proposed to explain the reaction between chloroformaldehyde and sodium hydroxide. The mechanism shows that only formic acid is formed during the reaction between chloroformaldehyde and sodium hydroxide.

KEYWORDS
Chloroformaldehyde, Sodium Hydroxide, Silver Nitrate, Ceric Ammonium Nitrate, Formic Acid.

INTRODUCTION
Properties and applications of chloroform are well documented in the literature.1−4 Thermo-chemical properties of chloroform have been developed and documented by Chase M.W. Jr. 5 Barta, Koons, et al. 6 studied details of thermodynamics of complex formation in chloroform and other organic compounds. Similar studies on complex formation in chloroform-benzene mixture are also documented.7 Alper, Peshekhodov, et al. 8 studied details of intermolecular interactions on chloroform-acetone system. Heat capacity, thermal and volumetric properties of chloroform have been studied by several researchers.9−13 The study of Mallick, 14 shows that nitric acid treatment on chloroform gives rise to chloroformaldehyde. Mallick, 15 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 sodium hydroxide solution at high temperature under reflux. It is believed that sodium hydroxide attacks the aldehyde group of chloroformaldehyde, but unlike Cannizzaro reaction only formic acid is formed with the liberation of chloride ion.

MATERIAL AND METHODS

• Preparation of 1:1 Nitric acid

50 mL Double distilled water is taken in a 250 mL beaker. 50 mL ACS grade concentrated nitric acid is added slowly to it. So 100 mL 1:1 nitric acid is prepared.

• 1(N)NH₄OH Solution

ACS grade concentrated NH₄OH solution is used to prepare 50 mL 1(N)NH₄OH solution using double distilled water.

• (N/2) NaOH Solution

ACS grade NaOH beads are used to prepare 100 mL (N/2) NaOH solution using double distilled water.

• (N/50) AgNO₃ Solution

ACS grade silver nitrate powder is used to prepare 100 mL (N/50) AgNO₃ solution using double distilled water.

• 1(N) Ceric Ammonium Nitrate Solution

ACS grade ceric ammonium nitrate powder is used to prepare 50 mL 1(N) ceric ammonium nitrate solution using double distilled water.

PROCEDURE

a. 40 mL ACS grade chloroform is taken in a reflux apparatus. 20 mL 1.1 Nitric acid is added to it. The mixture is heated at about 90°C for 45 min. under reflux. The heater is put off and the mixture is then cooled at room temperature under reflux. The 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. The bottom layer is chloroformaldehyde.14

b. 40 mL of the collected chloroformaldehyde is taken in a reflux apparatus; 40 mL of freshly prepared (N/2) NaOH solution is added to it. The solution is heated at about 90°C for 45 min. under reflux. The heater is put off and the mixture is then cooled at room temperature under reflux. The aqueous layer is separated using separating funnel.

c. 10 mL of the aqueous layer is taken in a 100 mL beaker. Add 2 drops of methyl red indicator. The solution turns pink indicating that the solution is acidic.

d. 10 mL of the aqueous layer is taken in another 100 mL beaker. 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) NH₄OH solution.

e. 10 mL of the aqueous layer is taken in another 100 mL beaker. Freshly prepared 2 mL (N/1) ceric ammonium nitrate solution is added to it. The solution remains colourless. No characteristic red colour for primary alcohol is observed.
PHOTOGRAPHS SNAPPED DURING TESTING OF PRIMARY ALCOHOL USING CERIC AMMONIUM NITRATE SOLUTION

Photograph 1: The Aqueous Solution obtained after Reaction between chloroformaldehyde and NaOH Solution

Photograph 2: The Mixture containing the Product Aqueous Solution and Ceric Ammonium Nitrate Solution. The faint Green Colour, as observed in the Photograph, is the Natural Colour of Ceric Ammonium Nitrate Solution. No Characteristic Red Colour of Primary Alcohol is observed

Photograph 3: The Mixture containing pure Ethanol and Ceric Ammonium Nitrate Solution. The Characteristic Red Colour is observed due to Ethanol

RESULTS AND DISCUSSION
Chloroform is colourless and possesses a characteristic sweet smell. After treatment with 1:1 nitric acid, chloroform is converted to chloroformaldehyde.14

The freshly prepared NaOH solution gives light yellow colour on addition of methyl red indicator, but after reaction with chloroformaldehyde the aqueous layer gives pink colour on addition of methyl red indicator. It is believed that formic acid is formed during the reaction between chloroformaldehyde and sodium hydroxide. The pink colour suggests that the amount of formic acid is enough to neutralize the NaOH solution.

The aqueous layer, collected after reaction between chloroformaldehyde and sodium hydroxide, gives white precipitate on addition of freshly prepared AgNO₃ solution and the precipitate is readily dissolved in ammonium hydroxide solution. The observation suggests that chloride ion (Cl⁻) is formed during the reaction between chloroformaldehyde and sodium hydroxide solution.

As chloroformaldehyde does not contain any α−H atom, hence it is expected that on reaction with sodium hydroxide (NaOH) chloroformaldehyde should follow Cannizzaro reaction to form formic acid or sodium formate and a primary alcohol. Accordingly, the aqueous layer containing the products should give characteristic red colour on addition of freshly prepared ceric ammonium nitrate solution due to the presence of primary alcohol. However, in this experiment the aqueous layer collected after reaction between chloroformaldehyde and sodium hydroxide solution showed a negative reaction with freshly prepared ceric ammonium nitrate solution. No characteristic red colour for primary alcohol is observed. The observation suggests that primary alcohol is not formed during reaction between chloroformaldehyde and sodium hydroxide.

The Proposed Mechanism is shown in the Fig. 1.

![Fig. 1: Proposed Mechanism of the Reaction between NaOH and Chloroformaldehyde](image)

CONCLUSION
Chloroformaldehyde, unlike other aldehydes with no α hydrogen, does not follow Cannizzaro reaction on treatment with NaOH solution. Only formic acid is formed with the liberation of chloride ion.
REFERENCES