

## 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  $\alpha - H$  atom follows Cannizzaro reaction with sodium hydroxide to form corresponding acid and alcohol. The present study shows that despite having no  $\alpha - H$  atom chloroformaldehyde 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 ceric ammonium nitrate test of alcohol group. However, reaction product mixture responds ferric chloride test of formic acid.

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<sup>1-4</sup>. Thermochemical 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 heat capacities of polar substances in chloroform

are also documented<sup>7</sup>. Ilchenko, et al.<sup>8</sup> studied details of intermolecular interactions on chloroform-benzene system. The study of Mallick<sup>9</sup> shows that nitric acid treatment on chloroform gives rise to chloroformaldehyde. Mallick<sup>10</sup> also showed that chloroformaldehyde on reaction with benzoyl peroxide produces chlorobenzyl formate.

The present paper deals with a detailed investigation 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

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. Preparation of 1(N)  $NH_4OH$  solution            Laboratory grade concentrated  $NH_4OH$  solution is used to prepare 50 ml 1(N)  $NH_4OH$  solution using double distilled water.

3. (N/2)  $NaOH$  solution    Laboratory grade  $NaOH$  beads are used to prepare 100 ml (N/2)  $NaOH$  solution using double distilled water.

4. (N/50)  $AgNO_3$  solution            Laboratory grade silver nitrate powder is used to prepare 100 ml (N/50)  $AgNO_3$  solution using double distilled water.

5. 1(N) ceric ammonium nitrate solution            Laboratory grade ceric ammonium nitrate powder is used to prepare 50 ml 1(N) ceric ammonium nitrate solution using double distilled water.

6. 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. The bottom layer contains chloroformaldehyde<sup>9</sup>.

7. 40 ml of the collected organic layer of chloroformaldehyde is taken in a reflux apparatus. Freshly prepared (N/2)  $NaOH$  solution is added drop-wise with shaking till the solution is alkaline. A litmus paper is used for this purpose. Then another 20 ml same (N/2)  $NaOH$

solution is added to it. The solution is heated to about 70°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. It is believed that the product of hydrolysis is distributed in both aqueous and organic layers.

8. 10 *ml* aqueous layer of *NaOH* treated chloroformaldehyde is taken in a 100 *ml* beaker. 2 *ml* freshly prepared (*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 10 *ml* organic layer of *NaOH* treated chloroformaldehyde followed by ammonium hydroxide solution as described above.

9. 10 *ml* aqueous layer of *NaOH* treated chloroformaldehyde is taken in a 100 *ml* beaker. 2 *ml* freshly prepared 1(*N*) ceric ammonium nitrate solution is added to it. No red colour is observed. Same observation is noticed when 2 *ml* 1(*N*) ceric ammonium nitrate solution is added to 10 *ml* organic layer of *NaOH* treated chloroformaldehyde as described above.

10. 5 *ml* organic layer of chloroformaldehyde (prepared as described in point no. 6) 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*<sub>3</sub> solution. Shake the mixture for few minutes. Yellow colour of *FeCl*<sub>3</sub> solution persists in aqueous layer of *FeCl*<sub>3</sub> solution.

5 *ml* organic layer of *NaOH* treated chloroformaldehyde (prepared as described in point no. 7) is taken in a 250 *ml* conical flask. Add 1 drop of phenolphthalein indicator. The solution remains colourless. Add 5 drops of 1% *FeCl*<sub>3</sub> solution. Shake the mixture for few minutes. Yellow colour of *FeCl*<sub>3</sub> solution vanishes forming colourless aqueous *FeCl*<sub>3</sub> solution.

## Results and Discussion

1. Chloroform is colourless and possesses a characteristic sweet smell. After treatment with 1:1 nitric acid, fraction of chloroform is converted to chloroformaldehyde<sup>9</sup>.

2. Both the aqueous layer and organic layer, collected after the reaction between chloroformaldehyde and sodium hydroxide, give white precipitate on addition of freshly prepared *AgNO*<sub>3</sub> solution and the precipitate is readily dissolved in ammonium hydroxide

solution. The observation suggests that chloride ion ( $Cl^-$ ) be formed during the reaction between chloroformaldehyde and sodium hydroxide.

3. As chloroformaldehyde contains no  $\alpha - H$  atom, it is expected that on reaction with sodium hydroxide ( $NaOH$ ) chloroformaldehyde should follow Cannizzaro reaction to form formic acid or sodium formate and methanol. So methanol should be present in both aqueous layer and organic layer. Hence, both the layers should give red colour on addition of freshly prepared ceric ammonium nitrate solution due to the presence of methanol. However, in the present study, neither aqueous layer nor organic layer, collected after the reaction between chloroformaldehyde and sodium hydroxide, gives red colour on addition of freshly prepared ceric ammonium nitrate solution. The observation suggests that methanol be not formed during the reaction between chloroformaldehyde and sodium hydroxide.

4. Organic layer, collected after the reaction between chloroformaldehyde and sodium hydroxide, is acidic as it remains colourless on addition of 1 drop of phenolphthalein indicator. After addition of  $FeCl_3$  solution, it is believed that formic acid diffuses from organic layer to aqueous layer to form colourless soluble complex  $(HCOOH)_3Fe$ . So yellow colour of  $FeCl_3$  solution disappears. The observation indicates that formic acid may be formed during the reaction between chloroformaldehyde and sodium hydroxide.

When the same experiment is carried out using organic layer, collected after the reaction between chloroform and nitric acid, yellow colour of  $FeCl_3$  solution persists. So it is believed that only chloroformaldehyde is formed during the reaction between chloroform and nitric acid.

5. The Fig.1 shows the proposed mechanism, illustrating the conversion of chloroformaldehyde to formic acid in presence of sodium hydroxide.

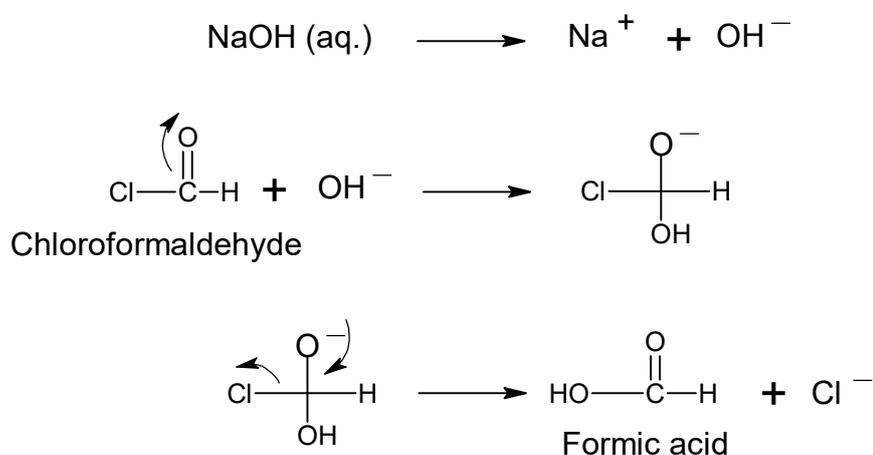


Figure.1 Proposed mechanism of the reaction between  $NaOH$  and chloroformaldehyde.

## Conclusion

Unlike other aldehydes with no  $\alpha - H$  atom, chloroformaldehyde, despite having no  $\alpha - H$  atom, does not follow Cannizzaro reaction on treatment with  $NaOH$  solution. Only formic acid is formed with the liberation of chloride ion during the reaction.

## References

- [1] J.A. Manion, "Evaluated Enthalpies of Formation of the Stable Closed Shell C1 and C2 chlorinated hydrocarbons", *J. Phys. Chem. Ref. Data*, vol. 31, (2002), pp. 123-172.
- [2] V. Majer, V. Svoboda, "Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation", Blackwell Scientific Publications, Oxford, (1985).
- [3] J.B. Pedley, R.D. Naylor, S.P. Kirby, "Thermochemical Data of Organic Compounds, 2<sup>nd</sup> edition", Chapman and Hall, New York, (1986).
- [4] W.E. Acree, Jr., "Thermodynamic properties of organic compounds: enthalpy of fusion and melting point temperature compilation", *Thermochim. Acta*, vol. 189, (1991), pp. 37-56.
- [5] M.W. Chase, M.W., Jr., "NIST-JANAF Thermochemical Tables", *J. Phys. Chem. Ref. Data*, vol. 9, (1998).
- [6] L. Barta, Z.S. Kooner, L.G. Hepler, G. Roux-Desgranges, J.P.E. Grolier, "Thermodynamics of complex formation in chloroform and 1,4-dioxane mixture", *Can. J. Chem.*, vol. 67, (1989), pp. 1225-1229.
- [7] J. -P. E. Grolier, G. Roux-Desgranges, M. Berkane, E. Wilhelm, "Heat capacities and densities of mixtures of very polar substances. 3. Mixtures containing either trichloromethane or 1,4-dioxane or diisopropylether", *J. Solution Chem.*, vol. 16, (1994), pp. 153-166.
- [8] O. O. Ilchenko, A.M. Kutsyk, Y.V. Pilgun et al., "Formation of molecular complexes in liquid benzene-chloroform mixtures examined by mid-IR 2D correlation spectroscopy and multivariate curve resolution", *Ukr. J. Phys.*, vol. 61, (2016) pp. 508-515.
- [9] A. Mallick, "A study on nitric acid treatment on chloroform", *Res. J. Chem. Environ.*, vol. 16, (2012), pp. 26-28.
- [10] A. Mallick, "A study on reaction between chloroformaldehyde and benzoyl peroxide", *Res. J. Chem. Environ.*, vol. 19, (2015), pp. 39-41.