

Synthesis of paraformaldehyde by Conversion of sodium (potassium or ammonium) formate salts by using ion exchange resin

Fathia¹. M.,I., Mubark², E.,O.

1 .Dr. Fathia Mohammed Ibrahim, National Center for Research/ Institute of Engineering Research and Materials Technology, e.mail Fatmhd25@yahoo.com

2. Pro. Mubark Elsayed Osman, University of Khartoum, Faculty of Science department of Chemistry.

Abstract:

The study aimed to prepare paraformaldehyde, and compare some of their physical and chemical characteristic with aldehyde (formaldehyde).

Formate salts solution (sodium or potassium) was converted into paraformaldehyde by transverse the mixture of formate salt into a column packed with hydrogen ion exchange resin (Amberlite-IRC50 (H)) to allow for exchange of sodium (or potassium) ions by protons (H^+). This was repeated three times, the eluate was left to stand to allow for evaporated of molecular form of solid paraformaldehyde as a white precipitate powder. It melt at ($140^{\circ}C$), (lit., $120-170^{\circ}C$), and infrared was recorded as ($C-O = 1260$, $C - O-C = 1083$, $C - H = 2921$ and $C - H_2 = 1469$)

The present of carbonyl group in paraformaldehyde, was chemically verified by positive reaction with acetone, acetamide, dinitro-phenylhydrazine and hydroxylamine, respectively. The paraformaldehyde obtained display all the chemical properties of aldehyde and readily reduces Tollen's, Benedict's and Fehling reagents, acting as reducing agents.

The results obtained (chemical reactions, infrared spectra and melting points) are in good accordance with expected and were found to be in agreement with these reported in the literature.

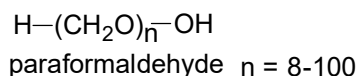
Keywords: Paraformaldehyde, Polyoxymethylene, formaldehyde polymer, formalin

Introduction:

Paraformaldehyde (PFA) is the smallest polyoxymethylene (a poly-acetal), the polymerization product of formaldehyde with a typical degree of polymerization of 8–100 units. Paraformaldehyde commonly has a slight odor of formaldehyde due to decomposition by dry heating. [1, 2, 3,4, 5, 6]

Paraformaldehyde is the solid form of liquid formaldehyde. Classified as a thermoplastic, this chemical compound exhibits the typical characteristics of similar polymers with linear long-chain polyoxymethylene glycols. In fact, this substance can be melted and cooled repeatedly and still retain these properties. [5,6]

Paraformaldehyde is obtained as a white powder when an aqueous solution of formaldehyde is evaporated. It melt between (120-170°C) and it was soluble in warm water. Formaldehyde is a water-soluble gas that forms methylene hydrate when hydrated. Methylene hydrate can be polymerized, which yields paraformaldehyde as a white precipitate. However, the addition of methanol is necessary to stabilize the polymerization process. [1, 2, 3] Its composition and molecular structure are uncertain (each molecule has a molecular weight of 30.03); its molecules may consist of long chains of alternated carbon and oxygen atoms produced by intermediate formation and polymerization of methylene glycol (HO-CH₂-OH), with alimentation of water.[1, 2, 3]



Like formaldehyde, paraformaldehyde is readily absorbed via the respiratory system, but is quickly metabolized to formate and excreted through the lungs or kidneys. It is also corrosive to skin and mucous membranes. [1, 2, 3,4]

Since paraformaldehyde is basically a condensed form of formalin, or aqueous formaldehyde, it possesses the same characteristics and uses. For example paraformaldehyde reacts with melamine, phenol, urea, vinylon, polycetal, diphenyl methane diisocyanate, terephthalic acid, resorcinol or other reactive agents, to produce resins used as binders in plywood and particleboard. [1,2, 3, 7]

Also it used as biological fixatives capable of inhibiting cellular degradation due to the breakdown of enzymes and bacterial replication.

These properties also make this compound useful as a fungicide and pesticide. It is also used in the manufacture of fertilizers, fluorescent lights, and certain chemicals used in photography and printing. It is also found in a wide variety of consumer goods, including vitamins, personal care products, and household cleaning products. Also it used in water decontamination, paints, and pharmaceuticals. [1,2, 3, 7]

Paraformaldehyde has documented uses as a disinfectant, fungicide, fixation reagent and in the preparation of formaldehyde. In fluorescence studies, paraformaldehyde has been used as a formalin fixative to fix cells and tissues. [8, 17]

Paraformaldehyde can be depolymerized to formaldehyde gas by dry heating [9] and to form a formaldehyde solution by water in the presence of a base or heat. The very pure formaldehyde solutions obtained in this way are used as a fixative for microscopy and histology.[15]

Once paraformaldehyde is depolymerized, the resulting formaldehyde may be used as a fumigant, disinfectant, fungicide, and fixative. Longer chain-length (high molecular weight) polyoxymethylenes are used as a thermoplastic and are known as polyoxymethylene plastic. It was used in the past in the discredited Sargenti method of root canal treatment. [10] As a formaldehyde releasing agent, paraformaldehyde is a potential carcinogen.[11, 12]

Formaldehyde is a gas. Its small molecules (HCHO, of which the -CHO is the aldehyde group) dissolve rapidly in water, with which they combine chemically to form methylene hydrate, HO-CH₂-OH. This is the form in which formaldehyde exists in aqueous solutions; its chemical reactivity is the same as that of formaldehyde. Methylene hydrate molecules react with one another, combining to form polymers known as paraformaldehyde (Fig. 1). The liquid known as formalin contains 37-40% of formaldehyde and 60-63% of water (by weight), with most of the formaldehyde existing as low polymers ($n = 2$ to 8 in the formula given in Fig. 1). Higher polymers (paraformaldehyde, n up to 100), which are insoluble and sold white powder. [13, 14, 15]

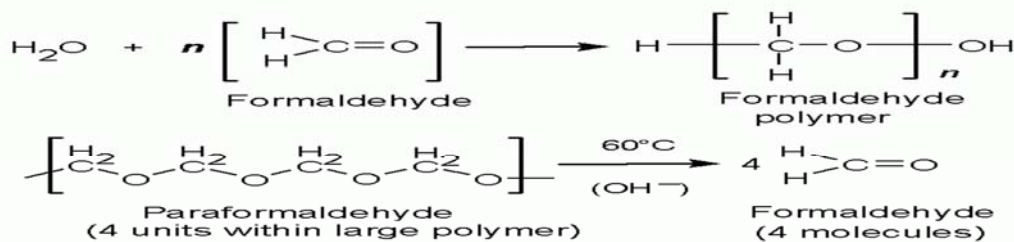


Fig. 1 Formation of formaldehyde polymers (above), and depolymerization of paraformaldehyde (below). **Fig. 1** Formation of formaldehyde polymers (above), and depolymerization of

To be useful as a fixative, a solution must contain monomeric formaldehyde (or methylene hydrate, as its major solute, or formalin is diluted with a buffer solution at physiological pH. [16] Hydrolysis of the polymers is catalyzed by the hydroxide ions present in the slightly alkaline solution). [17]

A solution of formaldehyde prepared from paraformaldehyde, is commonly used in fixatives for electron microscopy and in research applications. [18, 19]

Satisfactory ultrastructural preservation is, however, also seen in tissues fixed. [20, 21]

Materials and Methods:

Materials:

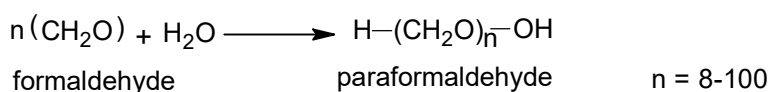
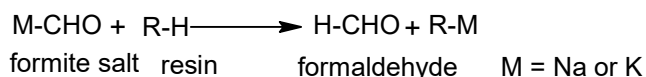
Sodium hydroxide, potassium hydroxide, sulphuric acid, formic acid, hydrochloric acid, distilled water, IRC-50 (H)) ion exchange resin , were used, as suggested by BDH, without further purification.

Methods:

Conversion of sodium (potassium or ammonium) formite salts into the paraformaldehyde by using ion exchange resin:

A column (a burette) was packed to about half its length, with resin IRC-50 (H). About 5 g of sodium salt prepared by the methods described above (2.3 and 2.4 and 2.9) were dissolved in distilled water and poured into the column already packed, to about half its length with Amberlite resin IRC-50 (H) to allow for exchange of sodium (or potassium) ions by protons (H^+). The eluate was treated, twice, in a familiar manner to ensure complete cationic exchange. The eluate was left to stand to allow for evaporated of molecular form of sold paraformaldehyde as a white powder. It melt at (149-152°C), (lit., 120-170°C), and infrared was

recorded as in fig., No.(1). The process can be outlined by the following equations:



Characterization of the paraformaldehyde:

1 g of paraformaldehyde prepared by the methods described above, were dissolved in distilled water and then filtered off. The resultant clear solution was added to acetaldehyde. The mixture was left few days; red precipitate was obtained. The same experiment was repeated using acetamide (yellow precipitate), acetone instead of acetaldehyde. Also the same experiment was repeated using formaldehyde instead of paraformaldehyde salts. The results are shown in the below table.

Results and Discussion:

Table 1. Characterization of the paraformaldehyde

Tests	paraformaldehyde	Formaldehyde	Melting point °C
Acetaldehyde	Red precipitate	-	139-143
Acetamide	Yellow precipitate	-	151-153

Acetone	Colorless solution	-	-
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Table 2. Melting point of formite salts and formite- 2,4-dinitrophenylhydrazone

Product	Melting point °C
Formite salt / Resin	149-152°C
Formite salt + DNPH	192°C
Formite salt / Resin + DNPH	144°C

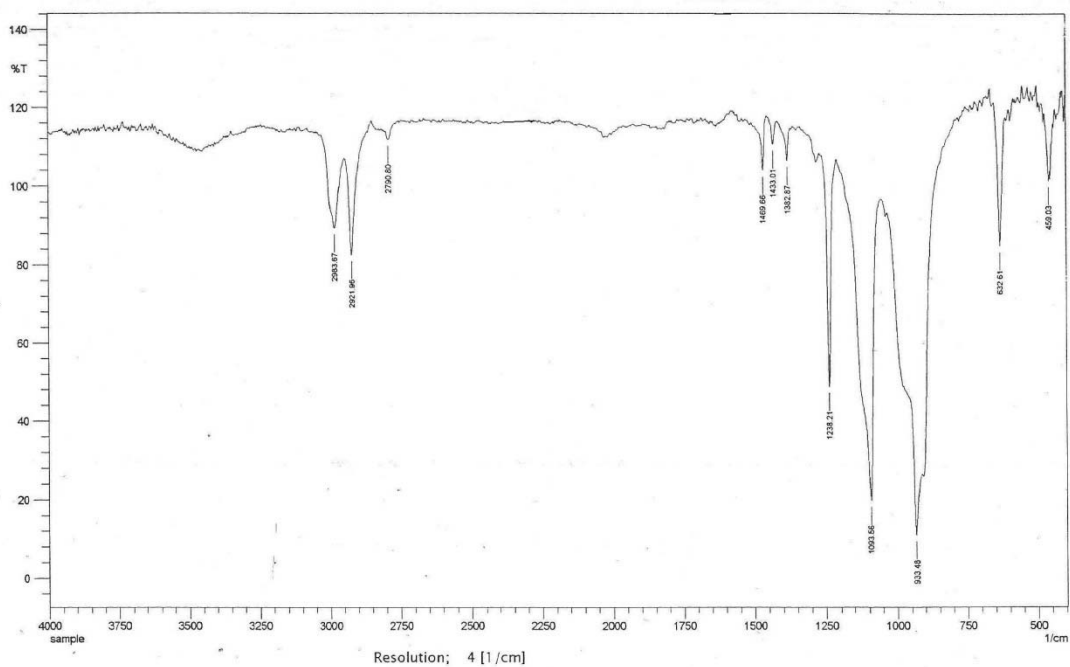


Figure 1. The infrared spectrum of formite salt/resin (parformaldehyde)

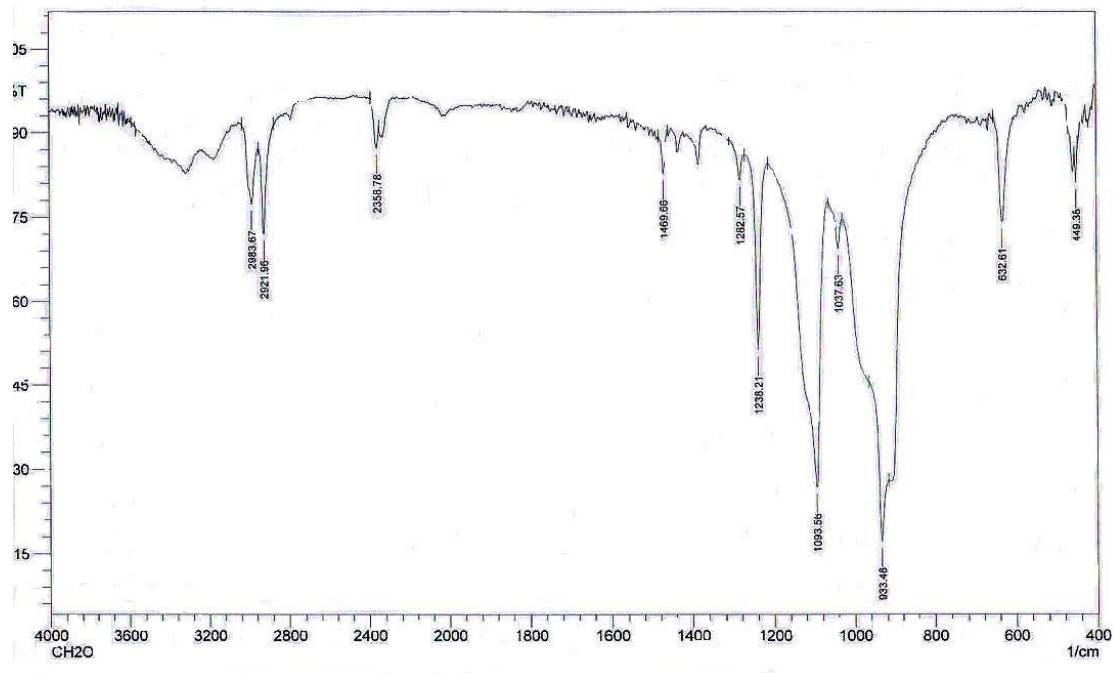


Figure 2. The infrared spectrum of solid formaldehyde (paraformaldehyde)

Table. 3. The infrared spectra of solid formaldehyde and, formite salt/resin

Solid formaldehyde (paraformaldehyde) ν / cm^{-1}	formite salt/resin (paraformaldehyde) ν / cm^{-1}	Assignment	Literature ν / cm^{-1}
2921	2921	C – H stretching	2800 – 2950
1469	1469	CH ₂	1465
1238	1238	C– O stretching	1000 – 1260
1083	1083	C– O – C	1000 – 1300



Conclusion:

In this study formite salts of sodium or potassium or ammonium were converted into paraformaldehyde by using ion exchange resin. Its infrared spectrum and melting point at 140°C indicated that the solution is paraformaldehyde. The results obtained (chemical reaction, infrared spectra and melting points) are in good accordance with theoretical and were found to be in agreement with these reported in the literature.

Results and Discussion:

Chemically paraformaldehyde was prepared by dissolving formaldehyde in water, its small molecules (HCHO), and combine to form methylene hydrate, HO-CH₂-

OH. Methylene hydrate molecules react with one another, to form polymers known as paraformaldehyde (n up to 100), as a white powder.

In the present work paraformaldehyde was prepared by allowing the formite salt solutions of (sodium, potassium and ammonium) to transverse columns packed with hydrogen ion exchange resin (Amberlite-IRC50 (H)).

To confirm the occurrence of the given reactions, the infrared has been determined and was found to be, (C-O = 1260, C – O-C =1083, C – H =2921 and C – H₂ = 1469) and the melting point has been determined (140°C), the results obtained were found to be in agreement with these reported in the literature. The paraformaldehyde obtained display all the chemical properties of aldehyde and readily reduces Tollen's, Benedect's and Fehlling reagents, acting as reducing agents. The results obtained are given in table and are in good accordance with theoretical.

Structurally the formite ion can be regarded as formaldehyde molecule in which one of the two hydrogen atom has been replaced by metal ion as the molecular formula (M-CHO) implies.

In aqueous solution the ion of formyl (M-CHO) it hydrolysis to formaldehyde:



Methylene hydrate

paraformaldehyde

The paraformaldehyde, like simple aldehyde and, yield additive compounds (cyanohydrin) with hydrocynic acid, and react with hydroxylamine to form oximes. In slightly acid solution, they react with excess phenylhydrazine to form phenylosazones, and osazones.



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