The Dicalcium Phosphate Dihydrate Fixator and Stabilizer of Glutaraldehyde

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Abstract: The dicalcium phosphate dihydrate (A) reacts with glutaraldehyde (B) in aqueous solution with a yield of 95%. The resulting product (C) is chemically stable. The obtained purity is checked by UV-Visible and the structure is discussed on the basis of the Infrared absorption FTIR. The reaction mechanism is explained by the approach of the hydroxyl group (-OH) of one of the aldehyde functions (-CO) of 1.5 dipentanal with the enolic form, which stabilizes the product (C). The reversible reaction is performed by mild oxidation of the compound (C) in aqueous medium at ambient temperature. The compound (A) is generated with high efficiency. The comparative spectral and thermography study confirms this result.

Key words: Dicalcium phosphate dihydrate, glutaraldehyde, oxidation, thermography.

1. Introduction

The Glutaraldehyde is a product used in the field of cold disinfection of surfaces and medical surgical instrumentation in large quantities [1-3]. In the light of studies on the bactericidal properties, the Glutaraldehyde destroys vegetative forms of bacterial species (lacking waxy wall) in at least five minutes and Microbacterium tuberculosis in ten minutes [3, 4]. Other important applications are stressed in various textile, paper, photography, tanning industries... [5, 6]. The physicochemical properties of the glutaraldehyde (volatility, miscibility, reactivity, etc.) [7, 8] show that it is harmful both to the health and the environment [9-13]. The risk of pollution is increased by the risk of explosion or fire [14]. Faced with such a dilemma (Production/pollution), the dicalcium phosphate dihydrate (CaHPO₄, 2H₂O) offers an easy way to stabilize the molecule by chemical fixation of glutaraldehyde OCH-(CH₂)₃-CHO. In fact, the role of fixator/stabilizer CaHPO₄, 2H₂O compound (A) is based on the approach of the hydroxyl group (-OH) of one of the aldehyde functions -CHO of CH₂-CH₂-OCH -CH₂-CHO (B) in solution, with a yield of 98. The resulting product of this connection is stable, the product (C). In addition, the mild oxidation with H₂O₂/H₂O of the compound (C) regenerates the compound (A) with an excellent yield (99%).

\[
\text{(CaHPO}_{4}\cdot\text{H}_2\text{O}) + \text{OCH-(CH}_2)_3\text{-CHO} \xrightarrow{\text{H}_2\text{O}} \text{OCH-(CH}_2)_3\text{-CH(OH)O(PO}_4\text{)Ca}
\]

2. Materials and Methods

The dicalcium phosphate dihydrated CaHPO₄, 2H₂O compound (A) is obtained by double decomposition of phosphoric acid H₃PO₄ (Merck) and the salt of calcium chloride CaCl₂ (Merck) in aqueous solution. After filtration, washing with distilled water followed by drying under hot air [15].
The Dicalcium Phosphate Dihydrate Fixator and Stabilizer of Glutaraldehyde

\[ \text{H}_3\text{PO}_4 + \text{CaCl}_2 \rightarrow (\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}) \]

Scheme 1  Synthesis reaction of the product A.

The CaHPO₄·2H₂O (A) appears in the form of white powder of spherical particles of 8 mm diameter (Fig. 1), on average with a variable porosity (Fig. 2).

The purity of the compound (A) is verified by UV-Visible (Fig. 3), the structural characterization is based on analysis by FTIR and confirmed by thermogravimetric study.

The fixation/stabilization reaction of the glutaraldehyde solution 20% (Anios, France) controlled by UV-Visible (Fig. 4). In a flask containing 250 ml of one mole of CaHPO₄·2H₂O was added 50 ml of OCH-(CH₂)₃-CHO (B) in aqueous solution under magnetic stirring. The reaction takes place at ambient temperature. The purity of the product (C) of red brick color is controlled by UV-Visible (Fig. 5), the yield of this reaction is 98%.

The reaction of H₂O₂/H₂O with the compound (C) under the same conditions allows to regenerate the compound (D) with an excellent performance (99%).

![Fig. 1  Microscope observation compound A.](image1)

![Fig. 2  Laser granulometry laser spectrum of compound A.](image2)

![Fig. 3  UV-Visible spectrum compound A.](image3)

![Fig. 4  UV-Visible spectrum compound B.](image4)

![Fig. 5  UV-Visible spectrum compound C.](image5)

The result is verified by UV-Visible spectral methods (Fig. 6) and infrared (Fig. 9). The confirmation is cemented by thermogravimetric study of the regenerated compound (D) CaHPO₄·2H₂O (Fig. 8).

Laser Granulometry: The apparatus used for particle size measurement is a type MALVERN MATERSIZER 2000 with the Scirocco as an accessory of dry dispersion.

Infrared absorption spectroscopy: The infrared absorption spectrophotometry: Nicolet 5700 series
Fig. 6  UV-Visible spectrum compound D.


Thermogravimetry: To study the thermal properties, samples of about 10 mg were measured using Seiko SSC 5200 thermoanalyzer (model 220 TG/DTA) with heating rates of 10-50 °C/min. flow rate of 100 ml/min.

3. Results and Discussion

There are two forms of dicalcium phosphate dihydrate with a ratio Ca/P = 1: [15]. Dicalcium phosphate dihydrate (DCPD or brushite) formula CaHPO₄, H₂O and its anhydrous salt of formula CaHPO₄. The thermal behavior of the product (E) regenerated by mild oxidation with hydrogen peroxide solution (10%) confirms the CaHPO₄·2H₂O. Indeed, the decomposition curve shown in (Fig. 7) shows an endothermic peak at 113.18 °C which corresponds to the end of the dehydration of the powder CaHPO₄, 2H₂O. Whereas the endothermic peak at 200 °C corresponds to the removal of water taken into the crystal lattice [16].

This phase is interpreted in the reaction (Schema 2), the confirmation is made by measuring the weight loss [17].

\[
\begin{align*}
\text{CaHPO}_4\cdot2\text{H}_2\text{O} & \rightarrow \text{CaHPO}_4 + \text{H}_2\text{O} \\
\text{A} & \rightarrow \text{E}
\end{align*}
\]

Scheme 2  Evolution of the structure of compound A between 100 °C and 200 °C

Two levels are distinguished on the path of the TG: Respectively, 7.30% and-12.37% of the total mass. The
retention of water in our product CaHPO₄·H₂O is of 19.67% in agreement with the theory [16], the percentage of the theoretical weight loss of CaHPO₄ is 20.92% at 300 °C. Between 300 °C and 500 °C is 4.34% with a peak at 399.5 °C on the curve of the TD. This change is explained by the evolution of CaHPO₄.

\[
2\text{CaHPO}_4 \rightarrow \text{Ca}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}
\]

Scheme 3  Evolution of the structure of compound A between 200 °C and 500 °C

The similarity of the thermal decomposition of products: the starting (A), regenerated (D) and the levels related to the evolution in terms of mass loss of these two products reinforce the results of spectral analysis. The comparative of the absorption of UV-Visible spectra (Fig. 3) and (Fig. 6) as well as Infrared absorption spectra FTIR of compounds (A) and (D) appear superimposed (identical) (Fig. 9). The spectral study of the compound (C) shows the chemical nature of the binding. The glutaraldehyde solution (B), controlled by UV-Visible reveals optimal optical density at 233 nm (Fig. 4) a characteristic of dipentanal 1.5. The compound (C) absorbs in the wavelength: 237 nm (Fig. 5) with a peak relatively wide. In addition, the FTIR spectrum of compound (C) indicates significant structural information (Fig. 10). PO₄ group appears with a good resolution (Fig. 10), compared to the starting spectrum of CaHPO₄·H₂O (Fig. 9). The spectrum of the molecule (C) is divided on one hand between the group CaPO₄·2H₂O of the compound (B) and the organic group -([CH₂]₃-CHO) introduced by the dialdehyde (B). The FTIR spectrum of CaHPO₄·H₂O (A) shows absorption bands at 3,538.7-3,489.6, 3,289.0-3,278.4, 3,164.6-3,018.1 cm⁻¹ which are characteristics of (O-H) stretching water, according

![TFIR spectrum Compound A and D.](image1)

![TFIR spectrum compound C.](image2)
Table 1  Comparison of TFIR compounds (C) and (A).

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The stretching vibration of -OH appears in the vicinity of 3,400 cm⁻¹ in our case. This value is a characteristic of -OH stabilized by the environment [17-18], relative to 3,600 cm⁻¹: If a (-OH) free. The aliphatic chain (- (CH₂)₃-) provides strong vibration: antisymmetric at 2,920 cm⁻¹ and symmetric at 2,850 cm⁻¹ distinctive of the aliphatic chain. However it should be noted in this frequency range lower additional bands which are active in infra red. This is the harmonic bands or combination of internal deformation modes of methylenes. This interpretation explains the broad shoulder starting around 2,700 cm⁻¹ and appends to the C-(OH) in terms of vibration. The vibrational band of valence (O - H) described since 1,895 appears at 3,300 cm⁻¹. This observation has been developed by other studies because of the physical dynamics of the group (O-H) (intramolecular and intermolecular chelate). Two broad bands at 3,530.3 and 3,149.2 cm⁻¹ in the compound (C) (Fig. 10) correspond to the vibration of water molecules but also the intermolecular behavior (O-H ... O = P), the chelant, and/or enolic forms of groups (-OH) in their molecular configuration [19-23].

The function (-CHO) confirmed by UV-Visible (highly diluted solution) may appear mostly in enolic form. The band at 1,400 cm⁻¹ characteristic of the double bond (C = C) confirms the proposed mechanism (schema 4) reported in the literature in the case of combined aldehyde functions [19-23].

![Scheme 4](image)

Scheme 4  Enolic form of compound C.
The band at 1,217 cm\(^{-1}\) may be characteristic of the skeleton (P-O-C) at the basis of linkage CaHPO\(_4\), H\(_2\)O and OCH-(CH\(_2\))\(_3\)-CHO. This structural part is still poorly understood, preliminary FTIR information in the chemistry of phosphines indicate the range 1,250-1,040 cm\(^{-1}\) [24, 25]. The treatment of compound (C) with a solution of H\(_2\)O\(_2\) at 10% generate the compound (A) with a very good performance (schema 4).

\[
\text{HOCH-CH=CH-CH2-CH(OH)O(PO4)Ca + H2O2} \rightarrow \text{CaHPO4·H2O + OCH-(CH2)3-CHO}
\]

Scheme 5  Oxidation reaction of compound D

The reversibility of the reaction gives the matrix CaHPO\(_4\), 2H\(_2\)O the property of stabilizer/fixator of the glutaraldehyde. On the basis of the reaction mechanism, the possible scenarios (schema 5), highlight the intramolecular bonds.

These bindings contribute to the stabilization of the product (C). They even explain the reversibility of the reaction. The approch of the molecule HO=OH following (schema 5) shows the evidence of this step.

4. Conclusions

Glutaraldehyde is a molecule that finds various applications. Consumed in large quantities in the medical and industrial fields. In addition, the molecule appears harmful to both health and environment. The CaHPO\(_4\), 2H\(_2\)O offers an easy and inexpensive way for the fixation and stabilization of glutaraldehyde. The attachment which is a reaction between the group (-OH) of CaHPO\(_4\), 2H\(_2\)O is interpreted in the skeleton (P-O-C) relatively stable. The stability of the molecule is enhanced by the enolic form of the function-free CHO. The mild oxidation by the diluted H\(_2\)O\(_2\) regenerates the starting molecule.

References


