ONE POT OBTENTION OF A TETRABUTYLAMMONIUM HYDROXIDE SOLUTION FOR IRONPORPHYRIN-OH⁻ INTERACTION STUDIES IN ORGANIC SOLVENTS

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In this work we report the obtention of a tetrabutylammonium hydroxide (TBAOH) solution in acetonitrile in a one pot process in order to study the interaction ironporphyrinOH⁻ in non-aqueous systems. All the reactions were carried out under dry argon atmosphere to prevent the contamination of the solution with CO_2, which leads to the formation of $(TBA)_2CO_3$.

Keywords: bioinorganic; coordination chemistry; basic solution in organic solvent.

1. INTRODUCTION

Ironporphyrins (FeP) have received great attention of researchers from the bioinorganic field[1]. Many efforts have been made in order to elucidate fundamental aspects of the structure, reactivity and reaction mechanisms of these complexes, which have potential application as catalysts in reactions of great industrial importance (e.g. epoxidation of olefins and hydroxylation of alkanes) and which are very important in biological processes[2,3]. Our research group has had great interest in studying the interaction between FeP and the axial ligand OH⁻, which is very important in the processes of FeP dimerization, hydroxide-FeP complex formation and oxidation-reduction reactions of the central metal ion[4-6]. However, the great majority of FeP that have been used as catalysts are only slightly soluble in water and studies of their interaction with NaOH in aqueous media lead to the dimerization of the non-hindered FeP[7]. Therefore, we have concentrated our efforts in order to obtain a non-aqueous tetrabutylammonium hydroxide (TBAOH) solution, which enables the study of the interaction FePOH⁻ in organic media without the occurrence of FeP dimerization.

TBAOH has been widely used as a basic non-aqueous titrant to analyse acidic materials and to differentiate acid mixtures[8]. A TBAOH solution may present impurities such as tributylamine, tetrabutylammonium carbonate ($(TBA)_2CO_3$) and dispersed silver oxide. The presence of amines does not contribute substantially to the results, particularly if sufficiently pure tetrabutylammonium iodide (TBAI) is used in the synthesis. In our case, however, the presence of amines may be undesirable since it may interfere in the FeP titrations. The most likely impurity is $(TBA)_2CO_3$, with dispersed silver dioxide being a suspect minor impurity.

We have chosen acetonitrile as the TBAOH solution solvent since it allows solubilisation of the reagents used in the synthesis and because it is easy to purify. The obtention of the TBAOH acetonitrile solution was based on the method described by Cundiff et al.[8], where modifications have been introduced in order to: a) prevent the formation of amines; b) prevent the contamination of the solution with CO_2, which leads to the production of $(TBA)_2CO_3$; c) provide good separation of silver oxide.

2. EXPERIMENTAL PROCEDURE

The starting TBAI was recrystallised from acetonitrile and dried under vacuum (~10 mmHg) at room temperature[9]. The

TBAI crystals were stored in dark flasks in a desiccator containing silica gel.

All the reactions were carried out in a single tube under argon atmosphere. A 10 mL centrifuge tube was adapted (Figure 1) so as to enable the introduction of solutions with the aid of gas tight syringes. In this way, it was not necessary to open the tube and the contamination of the system with CO_2 was avoided.

Figure 1. Centrifuge tube adapted with Teflon-silicone septum and two entries for microsyringes.

First of all, 2 mL of a NaOH 2 mol.L⁻¹ aqueous solution previously deaerated with argon were added to the adapted centrifuge tube containing AgNO₃ (190 mg) under argon atmosphere. This mixture was then stirred manually and by ultrasound, in order to favour the formation of an $Ag_2O.H_2O$ precipitate. After centrifugation, the supernatant was removed with the aid of a syringe. The precipitate was then consecutively washed with four portions of the following solvents: hot distilled water, methanol and acetonitrile. The washings consisted of the addition of 2 mL of the solvent to the $Ag_2O.H_2O$ precipitate, followed by manual and ultrasound stirring (5 minutes) and centrifugation (3 minutes). After the washings and removal of the supernatant with a syringe, the tube containing the $Ag_2O.H_2O$ precipitate under argon atmosphere was immersed in a NaCl-ice bath (T~ -8°C). Parallel to this procedure, TBAI (130 mg) was

dissolved in acetonitrile (8 mL) in another tube. This solution was kept under argon stream flow for 15 minutes and was then transferred to the tube containing the $Ag_2O.H_2O$ precipitate with the aid of a 10-mL gas tight syringe. The tube was then vigorously stirred (manually and ultrasound) at - $8°C$, in order to favour the formation of TBAOH in the solution and AgI as precipitate. This stirring process at low temperature was carried out for 60 minutes. Finally, this solution was centrifuged and the supernatant containing TBAOH in acetonitrile was transferred to previously deaerated 1-mL flasks containing an open top screw cap with a silicone-Teflon-faced septum. It is noteworthy that methanol and acetronitrile which were used in the $Ag_2O.H_2O$ precipitate washings had been previously dried, distilled and kept over 3 or 4Å molecular sieves. They were also purged with argon prior to the washings and so were the syringes used to add them into the tube.

Before being utilised in FeP titration studies, the TBAOH solution concentration was determined through neutralisation volumetry, by adding TBAOH solution to 500 mL of a HCl standard solution (~ 10^{-3} mol.L^{-1}) containing phenolphthalein as indicator, under argon atmosphere. The contents of the TBAOH solution 1 mL flask had its concentration determined on the same day it was used in an experiment and what remained unused in it was then discarded. The aliquots of TBAOH solution used in the FeP titrations were always removed from the flasks with the aid of syringes that had been previously purged with argon. The concentrations of the attained TBAOH/acetonitrile solutions were in the range of 10^{-3} to 10^{-2} mol.L^{-1}.

3. FINAL COMMENTS

• Purification of TBAI prior to its use in the synthesis was done to avoid amine impurities.
• The low temperature used in the experiment (~ -8°C) was necessary to prevent an eventual formation of amine, which may interfere in the FeP titrations.
• We preferred to prepare $Ag_2O.H_2O$ prior to its reaction with TBAI, rather than utilising the commercially available reagent since the latter may be contaminated with Ag_2CO_3.
• An excess of $AgNO_3$ is necessary to guarantee total precipitation of iodide as AgI.
• All the precautions were taken due to the low concentration of TBAOH in solution and its reactivity with CO_2.
• The consecutive washings of the $Ag_2O.H_2O$ precipitate with dry methanol and acetonitrile avoided the presence of water. Our concern was to guarantee that OH⁻ was the only ligand present in the solution.

Despite all the precautions, it is not possible to prevent the total absence of CO_2 and H_2O in the TBAOH solution. However, carrying out spectrophotometric studies involving FeP, more specifically Fe(TPP) (iron (III) mesotetraphenylporphyrin), and using TBAOH solution prepared through the procedure described above, we observed the formation of the FeTPP(OH)$_2$ complex[4], and not the formation of the FeP μ-oxo dimer, which is attained in aqueous alkaline media[7].

When the titration of a Fe(TPP) solution in 1,2-dichloroethane with aliquots of the TBAOH acetonitrile solution was followed by UV-Vis spectra, the appearance of an absorption band at λ = 576 nm, due to OH⁻ coordination to the FeP was observed[7] (Figure 2). At the same time, it was also possible to observe the disappearance of the band at λ = 510 nm and the shoulder at λ = 375 nm, due to Cl⁻ coordination to the FeP[7,10,11]. The number of OH⁻ ions that coordinates to Fe(TPP) (n) and the stability constant for the Fe(TPP)-OH⁻ complex (β_n) were calculated by the method developed by Iwamoto[4,12] and the values obtained were n = 2 and β_2 = 1.8 x 10^8 mol^{-2}.L^2. The EPR spectra of the Fe(TPP)(OH)$_2$ complex attained at the end of the titration of Fe(TPP) with TBAOH (Figure 3) displays a signal at g = 5.986,

which leads to the conclusion that the bis-hydroxide complex contains the Fe^{III} ion in its high-spin state. Such signal is highly symmetric, which is expected if OH⁻ ions are bonded to the Fe^{III} ion in the 5th and 6th coordination positions of this metal. We have discarded the formation of the μ-oxo dimer [Fe(TPP)]$_2$O upon TBAOH addition in this case because this complex does not present EPR signals. Furthermore, an absorbance band at λ= 612 nm, characteristic of the μ-oxo dimer[11], was not observed in the UV-Vis spectrum of Fe(TPP)⁺ in the presence of excess TBAOH (Figure 2D). Moreover, the blue-shift of the Soret band that occurs upon dimer formation was not observed for Fe(TPP)⁺ upon OH⁻ addition[11].
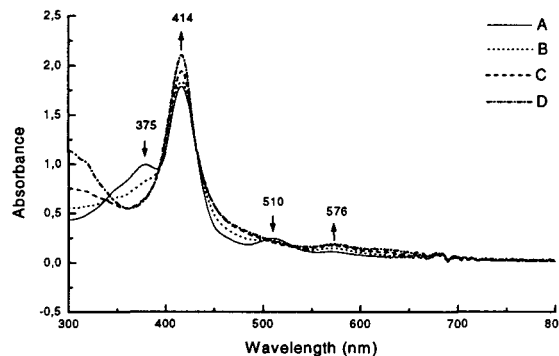
Figure 2. *Spectrophotometric titration of Fe(TPP)Cl in 1,2-dichloroethane (500 mL, 2.8 x 10^{-4} mol.L^{-1}, 1,4 x 10^{-7} mols FeP) with aliquots of 1,0 mL of TBAOH solution in acetonitrile (2.6 x 10^{-2} mol.L^{-1}). (A) initial Fe(TPP)Cl; after the addition of: (B) 1.0 x 10^{-7}; (C) 1.6 x 10^{-7} and (D) 3.4 x 10^{-7} mols of TBAOH.*
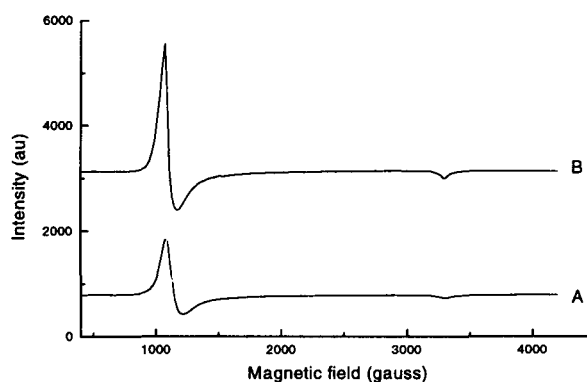
Figure 3. *EPR spectra of (A) Fe(TPP)Cl in 1,2-dichloroethane (100 mL, 8.0 x10^{-4} mol.L^{-1}); (B) (A) after the addition of 70 mL TBAOH solution (OH⁻/FeP molar ratio= 25). EPR spectrometer conditions: T = 4-5 K, Microwave potential = 4mW, modulation amplitude = 4.0 G, Microwave frequency = 9.260 GHz, gain = 2.5 x 10^2.*

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