



# Thermal decomposition and vibrational spectroscopic aspects of pyridinium hexafluorophosphate ( $C_5H_5NHPF_6$ )

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## ABSTRACT

Thermal decomposition and vibrational spectroscopic properties of pyridinium hexafluorophosphate ( $C_5H_5NHPF_6$ ) have been studied. The structure of the compound is better interpreted as having a cubic space group, based on Raman and infrared vibrational spectroscopy experiments and group theoretical correlation data between site symmetry species and the spectroscopic space group. The  $^{13}C$  NMR data shows three significant signals corresponding to the three chemical environments expected on the pyridinium ring i.e.  $\gamma$ ,  $\beta$  and  $\alpha$  carbons, suggesting that the position of the anion must be symmetrical with respect to the pyridinium ring's  $C_{2v}$  symmetry. The process of thermal decomposition of the compound using TGA methods was found to follow a contracting volume model. The activation energy associated with the thermal decomposition reaction of the compound is  $108.5 \text{ kJ mol}^{-1}$ , while the pre exponential factor is  $1.51 \times 10^9 \text{ sec}^{-1}$ .

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## 1. Introduction

Pyridinium hexafluorophosphate is a well-known precursor used in the synthesis of metal hexafluorophosphate salts [1]. These salts find applications as components of inhibitors, polymerization catalysts and flame retardants, but most importantly, in rechargeable batteries (lithium, potassium and sodium ion-batteries). The vibrational spectroscopic properties of pyridinium hexafluorophosphate have been studied before [1,2], but no mention of its thermal decomposition signature has been made and no correlation of vibrational spectroscopy experimental data with group theory was made to seek agreement and structural consistency with the space group for this important compound. It is possible to misinterpret vibrational spectroscopy data of a compound if the underlying space group is not verified by correlating Raman and IR experimental data with group theory [3]. For example, It has been shown that for the  $LiPF_6$  salt, Raman spectroscopy is a much more sensitive probe in situations where order/disorder or phase transition processes occur [4], a blind spot for pXRD. Phase transitions associated with order-disorder orientations in the pyridinium ring have also been observed for pyridinium hexafluorophosphate

( $C_5H_5NHPF_6$ ) and related compounds [5]. This is in contrast with the works of Copeland et al. [6], who could not observe any associated phase transitions for the same compound, and concluded that there is only one crystal structure for  $C_5H_5NHPF_6$ , being  $R-3m$  (166). However, the works of Cook [7], on the vibrational spectroscopy of pyridinium salts show that the pyridinium ring itself has a  $C_{2v}$  symmetry, and when interpreted from the perspective of  $C_5H_5NHPF_6$ , we should expect the presence of several triply degenerate phonon modes as part of the irreducible representations of the compound, emanating from the octahedral  $PF_6^-$  anion.

The structural data for a particular material has a strong dependence on the local symmetry of that material. Vibrational spectroscopy has been shown to be a better technique in detecting local symmetry changes as compared to pXRD which is very good in determining crystal structure for crystalline materials with well defined long range order [3]. It is clear that since bond energies are dependent on the bond properties, such as bond constants and atom positions, the underlying thermodynamic properties will depend on the data provided by techniques that accurately reflect a local structure.

The controversies in explaining phase transitions related to space group information in  $C_5H_5NHPF_6$  is analogous to the  $LiPF_6$  case, which has been shown to display a possible cubic phase at local symmetry level using Raman spectroscopy, while the long range cooperative symmetry is a trigonal based structure according to XRD data [3]. The effect of this on  $LiPF_6$  thermogravimetric data

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is profound, particularly when it comes to activation energy determinations, which are said to be reported with varying magnitudes [8]. This shows that a change in chemical composition or a possible phase transition, accompanied by a change in crystal structure of a material, will have an effect on the thermal properties of a substance.

In this work, we report the vibrational spectroscopy data of  $C_5H_5NHPF_6$  as correlated to group theoretical works and we show that the space group  $R-3m$  (166) as reported in literature [6] is not an accurate reflection of the compound, but rather an  $Fm3m$  (225) space group is a more representative alternative. We further show the thermal decomposition kinetics of  $C_5H_5NHPF_6$  and its thermal decomposition signature.

## 2. Experimental methods and materials

### 2.1. Synthesis of $C_5H_5NHPF_6$

A method proposed by Willmann et al. [9] for the synthesis of pyridinium hexafluorophosphate was used. Approximately 20 ml of aqueous  $HPF_6$  acid was added to a beaker and stirred continuously. About 10 ml of pyridine was added drop wise using a syringe while continuously stirring. The precipitate was filtered using a vacuum system and washed with water, and then the product was dried in an oven at 90° Celsius for 6 h.

### 2.2. Raman and infrared spectroscopy

The Ram II module (FT-Raman) mounted onto a vertex 70 FT-IR spectrometer (Bruker) was used to record the Raman spectra from 3500 to 0  $cm^{-1}$ . The sample was in a solid form. A 1064 nm wavelength excitation radiation was used and a 50 mW power setting and a wavenumber resolution of 4  $cm^{-1}$  was used throughout this study. FT-ATR Infrared reflectance spectra for powder samples were recorded with a Tensor T27 FT-IR spectrometer fitted with a Harrick Mvp-pro ATR cell. All reflectance spectra were recorded between 4000 and 500  $cm^{-1}$  with 32 scans and a resolution of 4  $cm^{-1}$ .

### 2.3. $^{13}C$ NMR analysis

For the  $^{13}C$  NMR, a Bruker NMR Spectrometer 500 was used for the analysis. The instrument was set for  $^{13}C$  dipolar dephasing (non-quaternary suppression) at room temperature (24.5 °C);  $^{13}C$  NMR (126 MHz, Deuterated methanol solvent)  $\delta$  244.94, 236.46, 224.39, 149.36, 141.47, 128.90, 53.68, 45.99, 33.77.

### 2.4. Thermal decomposition

#### 2.4.1. TG

About 20 mg sample of  $C_5H_5NHPF_6$  was analyzed on a modified TGS-2 Perkin Elmer TGA instrument. The instrument was enclosed within a dry glovebox and constantly purged with nitrogen gas. The sample was therefore heated from 30 to 600 °C at 10 °C/min under nitrogen purge gas.

#### 2.4.2. Thermal decomposition reactor-IR system

An in-house developed thermal decomposition reactor system coupled to a BOMEM MB 3000 spectrometer was used. The  $C_5H_5NHPF_6$  salt was loaded into a Ni sample pan, fitted into a tube reactor and then purged with a constant flow of laser-grade helium. A Hi-Tech Elements heater was used to heat the stainless-steel tube reactor to 350 °C. The evolved gas was captured at 20-min intervals with an Infrared gas cell fitted with zinc selenide windows, and a spectrum was recorded.

### 2.4.3. Kinetic studies

Decomposition kinetics studies were carried out using an isothermal method based on TG data obtained by using a dedicated TG instrument placed in a nitrogen glove box as in Section 2.4.1. Experimentally obtained data was fitted into various solid state kinetic models tabulated in the ICTAC kinetics committee recommendations by Vyazovkin et al. [10] and the best line fit using the least squares statistical evaluation technique was chosen. A confidence interval of 95% (Table 3) was used.

The following integrated rate equation was used:

$$g(\alpha) = [1 - (1 - \alpha)^3] = kt \quad (1)$$

In Eq. (1),  $\alpha$  is the extent of the reaction as derived from the global mass loss based on TG experimental data,  $k$  is the rate constant ( $s^{-1}$ ) and  $t$  is time (s). The extent of the reaction is calculated using Eq. (2).

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

Where  $m_0$  is the initial mass,  $m_t$  is the mass at a particular time and  $m_f$  is the final mass.

The dependence of the rate constant on temperature is based on the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

Where  $E_a$  is the activation energy in  $J \cdot mol^{-1}$ ,  $R$  is the universal gas constant ( $8.314 J \cdot mol^{-1} K^{-1}$ ) and  $A$  is the pre-exponential factor ( $s^{-1}$ ) associated with the rate of the reaction. The temperature  $T$  has units in Kelvin. The value of the rate constant,  $k$  at a particular temperature, was obtained from the slope of the  $g(\alpha)$  versus time curve (Eq. (1)).

## 3. Results and discussion

Raman and IR data of  $C_5H_5NHPF_6$  in Fig. 1 a and b showing the vibrational band frequencies and their assignments are given in Table 1. The 551 and 795  $cm^{-1}$  IR active bands belong to  $T_{1u}$  ( $\nu_4$  and  $\nu_3$  respectively). The  $T_{1u}$  is the only IR active mode from the octahedral  $PF_6^-$  anion in the compound; the others are contribution from the pyridinium ring. Previously, the vibrational band assignments for the  $C_5H_5NHPF_6$  were done by Mohamed et al. [2] and

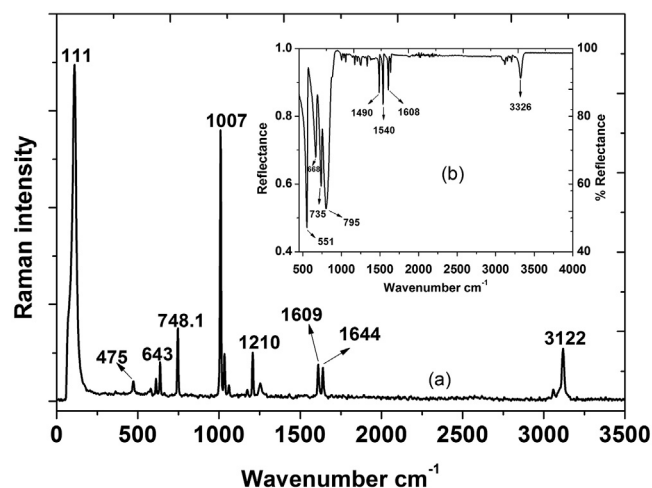


Fig. 1. Raman spectrum of  $C_5H_5NHPF_6$  (a) and FTIR-ATR spectrum of  $C_5H_5NHPF_6$  (b).

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