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The preparation and analysis of fluoro-polyphosphates by ^{19}F, ^{31}P, 2D ^{19}F–^{31}P HETCOR and 2D ^{31}P–^{31}P COSY NMR

Xiaodong Zhao [a,b], Long Zhu [b], Jianbin Huang [a,*], Xiujun Xu [b], Yong Pan [b]

[a] *Institute of Physical Chemistry, Peking University, Beijing 100871, PR China*
[b] *Procter & Gamble Co. Ltd., Beijing Technical Center, China and Miami Valley Laboratories, OH, USA*

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Abstract

A complex mixture of fluoro-polyphosphates (FPPs) and polyphosphates was prepared by heating a mixture of NaF and sodium tripolyphosphate (STPP) at 600 °C in nitrogen atmosphere. Two-dimensional ^{31}P–^{19}F heteronuclear correlation spectroscopy (HETCOR) NMR was developed in identifying the atomic connection between F and P in the mixed FPPs. ^{19}F, ^{31}P and ^{31}P–^{31}P correlation spectroscopy (COSY) NMR methods were employed to identify the components of the mixture and measure the chain length of each FPP ingredient. NMR results clearly demonstrated that the mixture contains four kinds of fluoro-phosphates with different chain length of polyphosphate, which are monofluoro-phosphate (MFP), monofluoro-dipolyphosphate (MFDPP), monofluoro-tripolyphosphate (MFTPP) and difluoro-tripolyphosphate (DFTPP). Other phosphates and polyphosphates also were found in the mixture.

Keywords: Fluoro-polyphosphate; ^{31}P–^{19}F HETCOR NMR; ^{31}P–^{31}P COSY NMR

1. Introduction

Fluorophosphates have been widely attracted great attention for industrial applications, such as electrochemical insert agents [1], fungicides, insecticides [2], nano-materials [3] and laser material [4,5]. As an important fluorophosphate in human daily life, sodium monofluorophosphate (MFP) has been extensively used in commercial dentifrices as an anti-cavity reagent [6]. Since MFP has similar phosphate-component with human tooth, so it has stronger affinity with the tooth, and can deliver sustaining anti-cavity performance. Based on this concept, fluoro-polyphosphates (FPPs), such as fluoro-dipolyphosphate (FDPP) fluoro-tripolyphosphate (FTPP) maybe deliver better anti-cavity performance than MFP since they have longer chain length of phosphate than MFP. MFP can be got easily by heating the mixture of NaF and sodium orthophosphate at 600–800 °C.

The objective of this study is to synthesize FDPP or FTPP by heating the mixture of NaF and pyrophosphate or STPP at high temperature. Maybe this reaction is very complex, many other byproducts will be produced when synthesizing them at a high temperature. Another objective of this work is to develop a suitable analytical method to identify the components of the product and further to optimize the reactive condition and understand the mechanism of this kind of reaction.

NMR is a powerful tool in identifying the components and structures of unknown substances, high-resolution solution ^{19}F [7–13] NMR, ^{31}P [3,14–17] NMR methods have been extensively used to study fluoride and fluorophosphates. It is a possible way to analyze the components of the product.

In this study, a mixture of FPPs were prepared by heating the mixture of NaF and STPP at 600 °C first, then we developed 2D ^{19}F–^{31}P HETCOR NMR method by using MFP as a sample. The peaks in ^{19}F NMR and ^{31}P NMR of FPPs were assigned by utilizing this method and finally the ingredients of FPPs were analyzed.

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* Corresponding author. Fax: +86 10 587 424 60.
E-mail address: zhao.sp.1@pg.com (X. Zhao).

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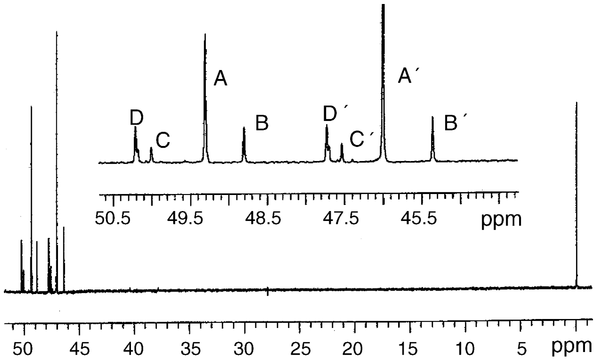


Fig. 1. ^{19}F NMR spectrum of the mixture (the chemical shift of NaF was set up as 0 ppm).

2. Result and discussion

2.1. ^{19}F NMR

HPLC has been used to analyze the components of MFP in the presence of phosphates [18]. However, maybe it is not a suitable method for this sample containing fluoro-polyphosphate due to its instability [19,20] in D_2O and no standard fluoro-polyphosphate sample available. ^{19}F NMR [21,22] provides an alternative method for the structural analysis. Fig. 1 shows ^{19}F NMR spectrum of the mixture. It is clear that in addition to the peaks from NaF (0 ppm) and MFP (A, A′), other six peaks (B, B′ and C, C′ and D, D′) were observed. Unfortunately, no references were found to help assigning all the peaks. It seems that the peak shapes and J coupling constants of B, B′ and C, C′ and D, D′ are very similar with A and A′, so it is possible that these peaks are from different FPPs with different chain length of polyphosphates.

2.2. ^{31}P NMR

^{31}P NMR [23,24] is another method to analyze the composition of phosphatic mixture. Fig. 2 shows the ^{31}P NMR spectrum of the sample. It is easy to assign the peaks at 2.37 and −2.99 ppm to MFP by comparing with a standard spectrum of MFP. It is also confirmed by the fact that the $J_{P–F}$ coupling constant is about 869 Hz. However, the spectrum is very complex. It is difficult to assign other peaks because the mixture contains unreacted STPP, orthophosphate (0 ppm) and pyrophosphate (−9.0 ppm) produced by the degradation of STPP, and polyphosphate produced by polymerization of STPP and FPPs. It is noticeable that the peaks in −14.49, −14.61 ppm and −20.17, −20.28 ppm are very similar shape. Norimasa Yoza reported minor peaks at about −15 ppm in his previous study [18], However, the peaks were not assigned because the peaks were very weak. Also, other similar peaks in −15.75, −15.86 ppm and −21.49, −21.60 ppm, −16.21, −16.31 ppm and −21.96, −22.06 ppm were found. In both ^{19}F NMR and ^{31}P NMR spectra, three pair unknown peaks appeared. This implies that the sample might contain three other fluoro-phosphates, in addition to MFP. It is important to have other evidences to confirm that the P atoms in ^{31}P NMR spectrum connect with F atoms in ^{19}F NMR spectrum.

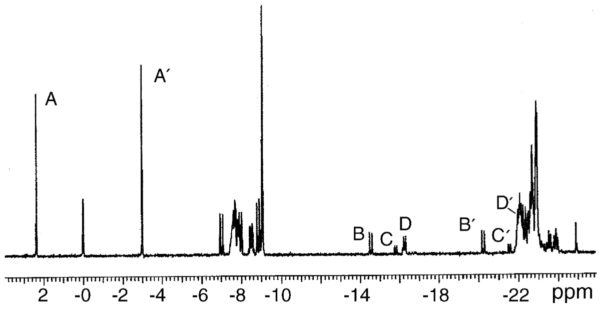


Fig. 2. ^{31}P NMR spectrum of the mixture (the chemical shift of Na_3PO_4 was set up as 0 ppm).

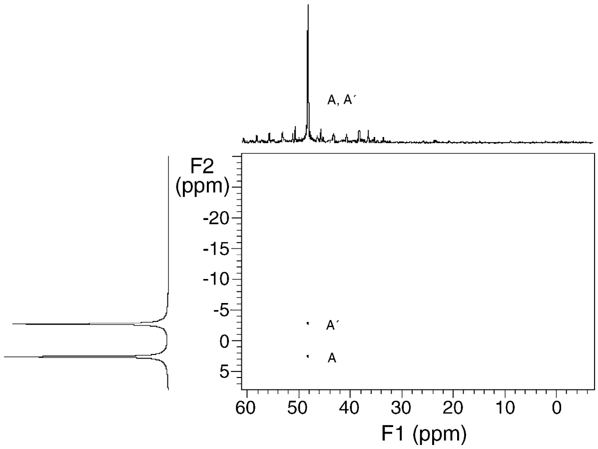


Fig. 3. 2D $^{19}F–^{31}P$ HETCOR NMR spectrum of MFP.

2.3. $^{19}F–^{31}P$ HETCOR NMR

$^{19}F–^{31}P$ HETCOR NMR spectrum like $^1H–^{13}C$ HMQC is the best way to establish the connectivity between P and F. In this study, MFP was used to develop the method. A large J

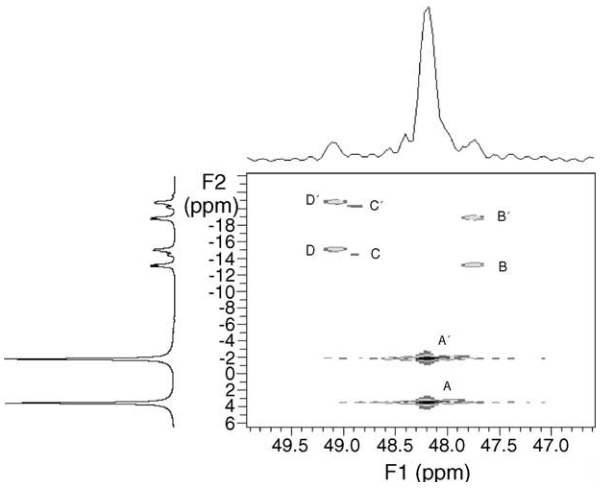


Fig. 4. 2D $^{19}F–^{31}P$ HETCOR NMR spectrum of the mixture.

Table 1
The coupling constant between F and P atom in ^{19}F NMR and ^{31}P NMR

Resonance	A–A′(MFP)	B–B′	C–C′	D–D′
J_{P-F} in ^{19}F NMR (Hz)	869 ± 2	918 ± 2	931 ± 2	931 ± 2
J_{F-P} in ^{31}P NMR (Hz)	872 ± 2	921 ± 2	930 ± 2	929 ± 2

coupling constant 900 Hz was set up in this NMR experiment because J_{P-F} is about 869 Hz.

Figs. 3 and 4 show the ^{19}F–^{31}P HETCOR NMR spectra of MFP and the mixture, respectively. Because the J coupling between P and F, two cross peaks were observed for MFP in Fig. 3. This indicates that it is reasonable to use this method to detect connectivity between P and F atom. In Fig. 4, four pairs correlation peaks (A, A′ and B, B′ and C, C′ and D, D′) were detected, the result means this sample contains four kinds of fluoro-phosphates, one pair (A, A′) of them is from MFP, other three pairs (B, B′ and C, C′ and D, D′) are from new unknown fluoro-phosphates. This spectrum proved that the peaks B, B′ and C, C′ and D, D′ in ^{19}F NMR connect directly with the ^{31}P peaks B, B′ and C, C′ and D, D′ in ^{31}P NMR, respectively. The J coupling interaction between F and P makes each peak both in ^{19}F NMR (Fig. 1) and ^{31}P NMR (Fig. 2) split into two peaks. The J coupling constants for J_{P-F} in ^{19}F NMR and for J_{F-P} in ^{31}P NMR are listed in Table 1.

It is obvious that the coupling constants J_{P-F} and J_{F-P} for each pair cross peak are nearly same. This is an another important evidence in demonstrating that B, B′ and C, C′ and D, D′ in ^{19}F NMR are directly connected to B, B′ and C, C′ and D, D′ in ^{31}P NMR spectrum. In addition, the coupling constants $J_{A-A'}$, $J_{B-B'}$ and $J_{C-C'}$ are not exactly the same. This implies that these resonances come from different FPPs. However, the chain lengths of these three FPPs cannot be estimated by using ^{19}F–^{31}P HETCOR NMR spectrum. A long distance ^{19}F–^{31}P correlative NMR experiment like ^{1}H–^{13}C hetero-nuclear multiple bond correlation (HMBC) was tried to measure the chain length of these fluoro-polyphosphates. Unfortunately, the cross peaks between F and indirect-connection P cannot be detected because the spin coupling interaction between F and P is too weak due to the long distances.

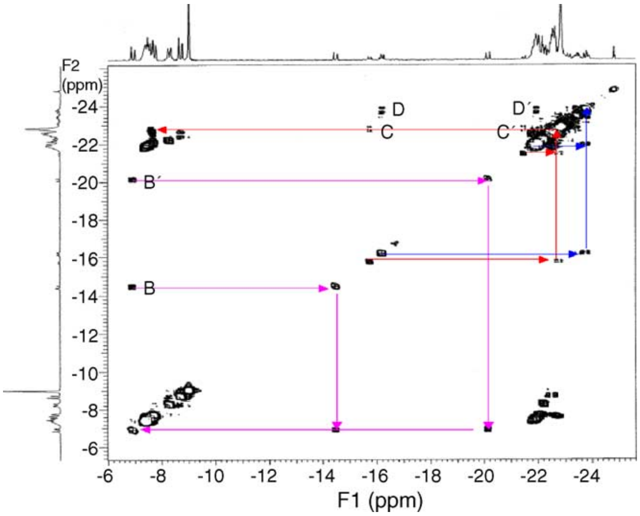
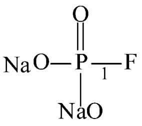
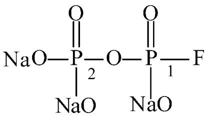
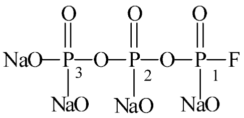
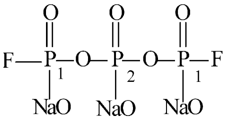


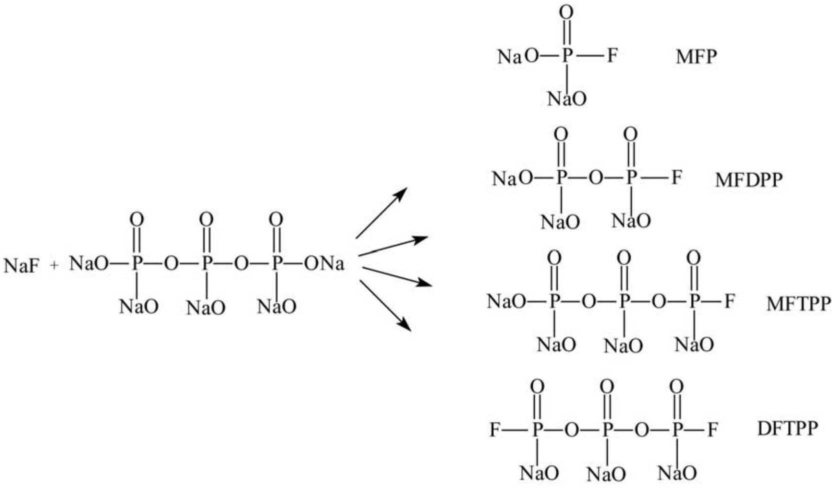
Fig. 5. 2D ^{31}P–^{31}P COSY NMR spectrum of the mixture.

2.4. ^{31}P–^{31}P COSY NMR

^{19}F–^{31}P HETCOR NMR spectrum clearly demonstrated the peaks B, B′ and C, C′ and D, D′ in ^{31}P NMR spectrums are

Table 2
The assignment of each fluoro-phosphates for ^{19}F NMR and ^{31}P NMR spectra

Ingredient	^{19}F (ppm)	^{31}P (ppm)	Split
 $\mathrm{NaO{-}\underset{NaO}{\overset{O}{P_1}}{-}F}$	47.0, 49.3	P1 (2.37, −2.99)	2
 $\mathrm{NaO{-}\underset{NaO}{\overset{O}{P_2}}{-}O{-}\underset{NaO}{\overset{O}{P_1}}{-}F}$	46.4, 48.8	P1 (−14.49, −14.61; −20.17, −20.28)	4
		P2 (−6.94, −7.07)	2
 $\mathrm{NaO{-}\underset{NaO}{\overset{O}{P_3}}{-}O{-}\underset{NaO}{\overset{O}{P_2}}{-}O{-}\underset{NaO}{\overset{O}{P_1}}{-}F}$	47.6, 50.0	P1 (−15.75, −15.86; −21.49, −21.60)	4
		P2 (around −23.0)	Not clear
		P3 (around −7.8)	2
 $\mathrm{F{-}\underset{NaO}{\overset{O}{P_1}}{-}O{-}\underset{NaO}{\overset{O}{P_2}}{-}O{-}\underset{NaO}{\overset{O}{P_1}}{-}F}$	47.7, 50.2	P1 (−16.21, −16.31; −21.96, −22.06)	4
		P2 (23.78, 23.88, 23.97)	3



Scheme 1. An approximate reactive equation for the reaction between NaF and STTP.

directly connected to F atoms. There must be four species that contain a F–P–O– group. Another way to know the chain length of these FPPs is to determine how many P atoms connected with the P next to F. ^{31}P–^{31}P COSY NMR [25–27] is a good method to establish connectivity between P atoms. The spectrum is shown in Fig. 5. According to the correlation between P atoms, all ^{31}P peaks due to FPPs can be assigned. Peaks B, B′ connect with a doublet ^{31}P peak at about −7.0 ppm. This suggests that B, B′ correspond to MFDPP; Peaks C, C′ connects with two ^{31}P peaks at about −23.2 and −7.7 ppm. That means C, C′ come from MFTPP; Peaks D, D′ connects with only one peak at about −23.9 ppm. Its chemical shift is different from B, B′. Based on the chemical shift and triplex split (see Fig. 5 F1 dimension, Fig. 2 is not very clear) of the peak at −23.9 ppm, we assign was these peaks to difluoro-tripolyphosphate. Final assignment for each peak is listed in Table 2.

In addition to peaks from FPPs, many other ^{31}P peaks appeared in Fig. 2, the peak in −9.0 ppm is from pyrophosphate. The broad peak in −7.7, −22.9 ppm maybe correspond polyphosphate. There are still many peaks that cannot be assigned due the lack of resolution. The data reflect the fact that the reaction between NaF and STPP is very complex during heating treatment. Not only many kinds of fluoro-phosphates are produced, but also degradation and polymerization of STPP occurs synchronously. The approximate reaction equation is listed as Scheme 1.

Based on these two 2D NMR spectra, some splits ^{31}P peaks in Fig. 2 can be explained clearly. For example, the peaks at −14.49, −14.61 ppm and −20.17, −20.28 ppm are from same P atom, which was split into two peaks by *J* coupling with F atom first and then the further split into four peaks by coupling indirectly connected P atoms. ^{31}P NMR and ^{31}P–^{31}P COSY NMR provides wealthy information about the composition of the phosphate mixture and the structure of each ingredient in solution. It is a potential method for the investigation of polyphosphate or FPPs hydrolysis dynamics. After assigning all ^{19}F and ^{31}P peaks connected with F atom, it is easy to quantify the level of each fluoro-phosphate by adding a suitable internal reference into the sample. The method will be useful for optimizing the reaction condition and understanding the reaction mechanism.

3. Conclusions

A mixture of fluoro-polyphosphates and polyphosphates was prepared by heating the mixture of NaF STPP with 1:1 molar ratio at 600 °C in nitrogen atmosphere. A new ^{31}P–^{19}F HETCOR NMR method was developed in identifying the structure of individual component in the mixture. All ^{19}F peaks in the ^{19}F NMR spectrum and ^{31}P peaks connected with F atom in the ^{31}P NMR spectrum were assigned by using 2D ^{31}P–^{31}P COSY and ^{31}P–^{19}F HETCOR NMR spectra. NMR results clearly showed that the mixture contained four kinds of fluoro-phosphates, MFP, MFDPP, MFTPP and DFTPP. Apart from fluoro-phosphates other ingredients, such as orthophosphate, pyrophosphate and polyphosphate were also found in the sample. This result demonstrated that the reaction between NaF and STPP was very complex during heating treatment (see editing in previous paragraph) not only many kinds of fluoro-phosphates produced, but also the degradation and polymerization of STPP happened synchronously. This result implies that ^{31}P–^{31}P COSY NMR and ^{19}F–^{31}P HETCOR NMR should be a powerful tool in the future to study the structure and hydrolysis dynamics of polyphosphate and fluoro-polyphosphate.

4. Experimental

4.1. Sample preparation

NaF, STPP and MFP were purchased from Aldrich Chemical Co. and used in the experiments without any further purification. The fluoro-phosphates mixture was obtained by heating a mixture of NaF and STTP with 1:1 molar ratio at 600 °C for 30 min at platinic pot in nitrogen atmosphere. The mixture was used for NMR experiments directly without any separation.

4.2. NMR experiment

4.2.1. ^{19}F and ^{31}P NMR experiments

The sample for NMR measurements was dissolved in D_2O (0.5% and pH 7.3). The spectra were recorded on a Varian Mercury plus 400 MHz NMR instrument at the frequencies of 162.0 MHz for ^{31}P and 376.5 MHz for ^{19}F. To avoid the hydrolysis of the sample, no internal standards were added. The chemical shift for ^{31}P NMR and ^{19}F NMR was referenced at 0 ppm for Na_3PO_4 and NaF solution, respectively. All NMR experiments were performed at room temperature.

4.2.2. ^{31}P–^{19}F HETCOR NMR experiment

The spectral widths of the F_2 (^{31}P) and F_1 (^{19}F) dimensions were 6.4 and 28.6 KHz, respectively. Each collected datum set contained 512(t_1), 1024 (t_2) data points. The data set were linearly predicted to 1024, 1024 data points. Ninety-degrees pulse length was 12.5 μs for ^{31}P and 15.0 μs for ^{19}F. Recycle delay was 5 s. Number of acquisition was 16. *J* coupling of ^{19}F–^{31}P was set up as 900 Hz.

4.2.3. ^{31}P–^{31}P COSY NMR experiment

The spectral widths of F_1 and F_2 dimensions were both 6.4 kHz. Each data set contained 256(t_1), 1024 (t_2) data points. The data set were linearly predicted to 1024, 1024 data points. Ninety-degrees pulse length was 12.5 μs, recycle delay was 5 s. Number of acquisition was 16.

Acknowledgments

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