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Gas-phase on-line generation and infrared spectroscopic investigations of polyphosphazenes, $(NPX_2)_3$ where X = F, Cl and Br

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Abstract

Gas-phase infrared spectra of polyphosphazenes (phosphonitrilic halides trimer), $(NPX_2)_3$ where X = F, Cl and Br have been recorded. The molecules were generated for the first time by an on-line process using solid $(NPCl_2)_3$ as a precursor passed over heated sodium fluoride and potassium bromide at about 550 and 700 °C for $(NPF_2)_3$ and $(NPBr_2)_3$ production, respectively.

The products were characterized by the infrared spectra of their vapors. The low-resolution gas-phase Fourier transform infrared spectra reported for the first time show strong bands centered at 1295, 1215 and 1200 cm^{-1}, assigned to $\nu_7(E')$, in plane P—N stretching mode of $(NPX_2)_3$, where X = F, Cl and Br, respectively.

Keywords: Gas-phase; On-line generation; Polyphosphazenes; Infrared; Phosphonitrilic halides trimer

1. Introduction

Polyphosphazenes or phosphonitrilic halides trimer, $(NPX_2)_3$ where X = F, Cl and Br were prepared long time ago. The synthesis of the fluoro analogues, $(NPF_2)_3$ was first made in 1956 and the bromo compound $(NPBr_2)_3$ was prepared in 1960, where the chloro analogues was made much earlier in 1924. The basic preparation for the laboratory and industrial scales of the chloro analogue was applied under the following reaction: $n\text{PCl}_5 + n\text{NH}_4\text{Cl} \rightarrow (\text{NPCl}_2)_n + 4n\text{HCl}$ using the appropriate solvents at about 120–150 °C [1]. By varying the conditions, yields the cyclic trimer or tetramer and the other oligomers can be optimized and the compounds can be separated by the fractionation.

Analogues bromo compounds may be prepared in the same manner, except that bromine must be added to suppress the decomposition of the phosphorus penta-bromide. The analogues fluoro can be prepared indirectly by fluorination of the chloro analogues [1].

The cyclic trimer $(NPF_2)_3$ has an accurately planar six-membered ring (D_{3h} symmetry) in which all six P—N distances are equal. Most other trimers, $(NPCl_2)_3$ and $(NPBr_2)_3$, are almost planar (pseudo chair structure). The planarity of the ring, the equal P—N bond distances, the shortness of the P—N bonds and the stability of the compounds suggest the delocalization behavior [1,2].

The geometry for $(NPF_2)_3$ are as follows: P—N 1.56 Å, P—F 1. 51 Å, ∠NPN 121°, ∠PNP 119° and ∠FPF 99° where the geometry for $(NPCl_2)_3$ are as follows: P—N 1.58 Å, P—Cl 1.97 Å, ∠NPN 118.4°, ∠PNP 121.4° and ∠ClPCl 102° [2] (Scheme 1).

In the late sixties of the last century, two spectroscopic papers were published regarding the phosphonitrilic halides trimer, $(NPX_2)_3$ where X = F, Cl and Br but in the liquid and crystal states [3,4]. The first paper was published by Manley and Williams who recorded the infrared spectra of $(NPBr_2)_3$ and $(NPCl_2)_4$ in the range 40–3000 cm^{-1} and the materials were either presented in CCl_4 solutions or in solid state [3]. Their Raman data indicated that $(NPBr_2)_3$ in solution has D_{3h} symmetry, but in the crystal form showed a slight deviation from D_{3h} to C_{3v} symmetry, as in $(NPCl_2)_3$. The fundamental frequencies of both $(NPCl_2)_3$ and $(NPBr_2)_3$ in comparison

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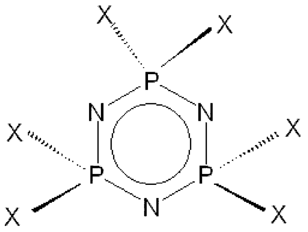

$(NPF_2)_3$: P-N 1.56Å, P-F 1. 51Å, ∠NPN 121°, ∠PNP 119°, and ∠FPF 99°
$(NPCl_2)_3$: P-N 1.58Å, P-Cl 1.97Å, ∠NPN 118.4°, ∠PNP 121.4° and ∠ClPCl 102°
$(NPBr_2)_3$: P-N 1.58Å, P-Br 2.12Å, ∠NPN 117.3°, ∠PNP 123.2 and ∠BPBr 103.2°

Scheme 1. The schematic resonance structure of $(NPX_2)_3$ where X = F, Cl and Br showing the delocalisation of π-bonding.

with $(NPF_2)_3$ were assigned on the basis of D_{3h} symmetry [3]. The second paper was published by Stahlberg and Steger who reported the infrared spectra of triphosphonitrilic chloride bromide, $P_3N_3Cl_nBr_{6-n}$ where $n = 0$–6, between 200 and 4000 cm^{-1} in the solid state [4]. The Raman spectra were recorded for the previous species with solid samples and for $P_3N_3Cl_5Br$ only in solution including the polarization measurements. The authors reported that the decrease of symmetry has little effect on the spectra because the P–Cl and P–Br bonds are very similar. But the effects surpass those of the crystal symmetry, C_{3v} as known for $P_3N_3Cl_6$ and $P_3N_3Br_6$ [4].

In 1970, Emsley reported the infrared and Raman spectra of the triphosphonitrilic fluoride chloride, $P_3N_3F_nCl_{6-n}$ where $n = 0$–6, between 300 and 2500 cm^{-1} including the related $P_3N_3Cl_6$ and $P_3N_3F_6$ compounds [5]. The solids $P_3N_3Cl_6$ and $P_3N_3FCl_5$ were studied as Nujol mulls and in the liquid state as liquid films; $P_3N_3F_6$ was studied in CS_2 and CCl_4 solutions above 650 cm^{-1} and as the vapors below 650 cm^{-1} [5].

Schnöckel and co-workers recorded the matrix isolation infrared spectrum of $P{\equiv}N{=}O$ species ($C_{\infty v}$) in the Argon atmosphere [6,7]. Both fundamental stretching, N=O and $P{\equiv}N$, vibrations were observed at 1754.7 and 865.2 cm^{-1}, respectively.

Atkins and Timms recorded the matrix isolation infrared spectrum of $(PN)_3$ species (D_{3h} symmetry) in the Krypton atmosphere [8]. Both e′ (P=N stretch) and e′ (P–N stretch) frequencies were observed at 1137 and 718 cm^{-1}, respectively. The work was extended and confirmed by Schnöckel and co-worker who recorded the matrix isolation infrared spectrum of only one fundamental e′ (P=N stretch) in the Argon atmosphere at 1141 cm^{-1} [9]. The matrix isolation infrared frequency of the elusive species $P{\equiv}N$, which was produced from the trimer, has been observed at 1323 cm^{-1} [8,10].

It can be noticed from the literature survey that, there is no gas-phase on-line generation and infrared spectroscopic investigation reported in the literature before for the polyphosphazenes compounds, $(NPX_2)_3$ where X = F, Cl and Br. This paper investigates the first attempt of gas-phase on-line production of polyphosphazenes, $(NPX_2)_3$ where X = F and Br using $(NPCl_2)_3$ as a starting material passed over heated sodium fluoride and potassium bromide at about 550 °C and 700 °C for $(NPF_2)_3$ and $(NPBr_2)_3$ production, respectively and the products were characterized by the infrared spectra of their vapors. Also, semi empirical calculations have been performed on $(NPBr_2)_3$ based on the D_{3h} symmetry.

2. Experimental

The first step was to optimize the production conditions of the chloro analogue, $(NPCl_2)_3$, before attempting to observe the following analogues, $(NPF_2)_3$ and $(NPBr_2)_3$.

The $(NPCl_2)_3$ solid material (Fluka, 99.99%) was heated alone in the vacuum line to about 106 °C using heating tape in order to obtain enough vapor pressure and recording the gas-phase infrared spectrum of this starting material. Then, this vapor was used and passed directly via a vacuum line over the chosen heated salt by an on-line process into an IR cell in order to produce $(NPF_2)_3$ and $(NPBr_2)_3$. The remaining conditions were slow flow, 2 cm^{-1} resolution and under 0.4–0.5 Torr pressure. The synthetic reaction routes for the preparation of $(NPF_2)_3$ and $(NPBr_2)_3$ can be written as follows:

$$(NPCl_2)_{3(g)} + 6NaF_{(s)} \xrightarrow{550\,^{\circ}C} 6NaCl_{(g)} + (NPF_2)_{3(g)}$$

$$(NPCl_2)_{3(g)} + 6KBr_{(s)} \xrightarrow{700\,^{\circ}C} 6KCl_{(g)} + (NPBr_2)_{3(g)}$$

The salts containing halogens used in these experiments were obtained from Aldrich with GR purity. The products from these reactions were passed directly into an IR cell (15 cm path length) fitted with two KBr windows.

The KBr optics is used to cover the conventional medium region of the FTIR Spectrometers (400–4000 cm^{-1}) due to the noninterference of KBr bond with the recorded spectra of that region.

The distance between the heated furnace and the IR cell was about 3 cm.

In order to avoid any disproportionation or polymerization, the IR cell was heated to about 200 °C with heating tape. The vacuum line system was pumped out via a liquid nitrogen trap with a rotary pump (ILMVAC) displacing 23 m^3 h^{-1}. The infrared spectra were recorded on a JASCO 300E FTIR spectrometer with a resolution of 2 cm^{-1}. Similar experimental setup can be seen in our previous work which was focused on the gas-phase on-line preparation and the infrared spectroscopic investigation of phosphoryl halides, POX_3 where X = F, Cl, Br and I [11].

3. Results and discussion

It should be pointed out here first, that there are 20 fundamental modes of vibrations regarding the $(NPX_2)_3$ molecules based on the D_{3h} symmetry.

The fundamental symmetry modes of vibration can be divided as follows:

$$4A'_1 + 2A'_2 + 1A''_2 + 3A''_2 + 6E' + 4E''$$

where the A'_1 and E'' are Raman active only, A''_2 is infrared active only, E' is active in both infrared and Raman and A'_2 and A''_1 are in active in both effects. The assignments of the recorded gas-phase infrared spectra are based on the D_{3h} symmetry.

Second, it should be mentioned also that a complete halogen exchange reaction between $(NPCl_2)_3$ gas and the solid NaF or KBr by an on-line process to produce $N_3P_3F_6$ and $N_3P_3Br_6$, respectively, is in general far from being trivial due to the appearance of the precursor bands under the applied gas-phase on-line production conditions. Nevertheless, we could observe some of the most characterized fundamental modes of $N_3P_3F_6$ and $N_3P_3Br_6$ in the gas-phase within the range of the spectrometer used.

Fig. 1 shows the gas-phase infrared spectrum of $(NPCl_2)_3$ in the range (400–1300 cm^{-1}). This spectrum was the result of heating $(NPCl_2)_3$ solid material only in the vacuum line to about 106 °C in order to record the gas-phase infrared spectrum of this starting material before generating $(NPF_2)_3$ and $(NPBr_2)_3$ compounds by an on-line process. Six bands centered at 1215, 671, 621, 562, 540 and 410 cm^{-1} were observed. The first band centered at 1215 cm^{-1} is assigned to $\nu_7(E')$, in plane P–N stretching mode of $(NPCl_2)_3$. This band can be compared with the similar mode observed in the liquid and solid $(NPCl_2)_3$ which has a frequency of 1226 and 1210 cm^{-1}, respectively [3,12,13]. The band has a PR type structure and the two sides frequencies are at 1232 and 1206 cm^{-1}. The observed frequency at 1215 cm^{-1} lies within the acceptable range. The second band at 621 cm^{-1} is assigned to $\nu_{14}(A''_2)$, the ring deformation, out of ring plane. This band can be compared with the same mode observed in solid $(NPCl_2)_3$ which has a value of 601 cm^{-1} [13]. It is well known that there could be a shift in the band position between the gas-phase and the solid states. The shift of about 20 cm^{-1} is justified and acceptable.

The third band at 540 cm^{-1} has been assigned to the $\nu_{15}(A''_2)$, the P–Cl_2 asymmetric stretch in plane vibration of $(NPCl_2)_3$.

This band can be compared also with the similar modes observed in solid and liquid form of $(NPCl_2)_3$ which has a frequency of 540 and 544 cm^{-1}, respectively [13,12]. Our recorded results are consistent and very close and some frequencies are identical with those reported earlier [12,13]. The remaining small bands at 671, 562 and 410 cm^{-1} are not assigned and could be due to the combination frequencies.

Having confirmed the existence of gas-phase infrared spectrum of $(NPCl_2)_3$, the next step was to record the gas-phase infrared spectrum of $(NPF_2)_3$ using $(NPCl_2)_3$ as a starting material by an on-line process of preparation.

Fig. 2 shows the gas-phase infrared spectrum of $(NPF_2)_3$. This spectrum was the result of passing a controlled vapor pressure of $(NPCl_2)_3$ precursor over heated sodium fluoride at about 550 °C. Three characteristic bands were observed at 1295, 980 and 868 cm^{-1} in the range 600–1500 cm^{-1}. The first band centered at 1295 cm^{-1} is assigned to $\nu_7(E')$, in plane P–N stretching mode of $(NPF_2)_3$.

This band can be compared with the similar mode observed in the solid state of $(NPF_2)_3$ which has a value of 1305 and 1300 cm^{-1}, respectively [14,15]. The band has a PR type structure as in the previous chloro analogues and the two sides frequencies are at 1310 and 1271 cm^{-1}.

This results is consistent with the expectation and the band is shifted to higher frequency when fluorine replaces the chlorine in $(NPCl_2)_3$ in order to form $(NPF_2)_3$.

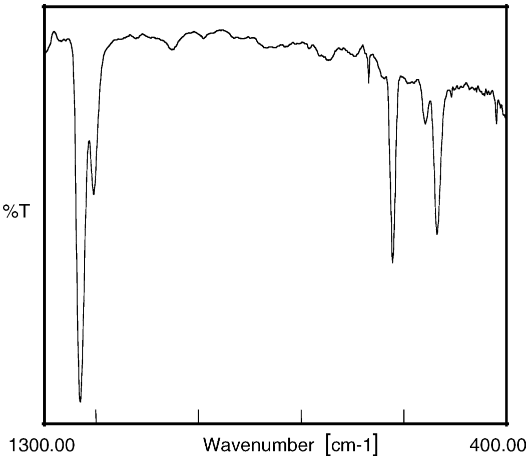

Fig. 1. Gas-phase infrared spectrum of $(NPCl_2)_3$. Three characteristic bands were observed at 1215, 621 and 540 cm^{-1} in the range 400–1300 cm^{-1}.

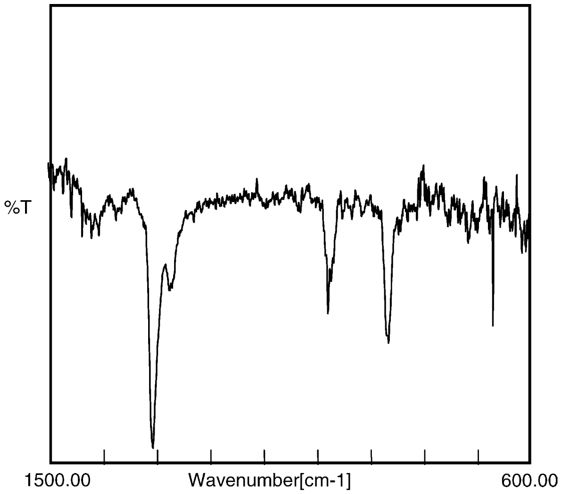

Fig. 2. Gas-phase infrared spectrum of $(NPF_2)_3$. Three characteristic bands were observed at 1295, 980 and 868 cm^{-1} in the range 600–1500 cm^{-1}.

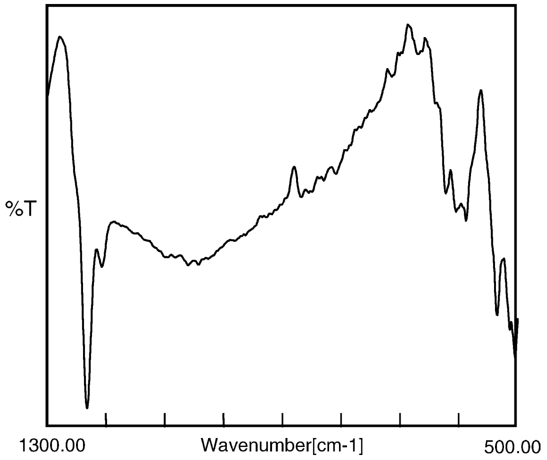

Fig. 3. Gas-phase infrared spectrum of $(NPBr_2)_3$. Three characteristic bands were observed at 1200, 560 and 532 cm^{-1} in the range 500–1300 cm^{-1}.

The second band at 980 cm^{-1} is assigned to $\nu_{14}(A_2'')$, the ring deformation, out of ring plane. This band can be compared with the same mode observed in the solid $(NPF_2)_3$ which has a value of 975 cm^{-1} [14].

The third band at 868 cm^{-1} has been assigned to $\nu_{15}(A_2'')$, the P–F_2 asymmetric stretch in plane vibration of $(NPF_2)_3$. This band can be compared with the similar mode observed in the solid state of $(NPF_2)_3$ which has a value of 860 and 865 cm^{-1}, respectively [14,15]. It can be deduced that the reported results are very consistent with the previous recorded results.

Fig. 3 shows the gas-phase infrared spectrum of $(NPBr_2)_3$ in the range 500–1300 cm^{-1} This spectrum was the result of passing a controlled vapor pressure of $(NPCl_2)_3$ precursor over heated potassium bromide at about 700 °C.

The first small band centered at about 1200 cm^{-1} is tentatively assigned to $\nu_7(E')$, in plane P–N stretching mode of $(NPBr_2)_3$. This band can be compared with the similar mode observed in the liquid and solid form of $(NPBr_2)_3$ which has a frequency of 1173 and 1180 cm^{-1}, respectively [3,4]. The shift range between the previous reported and the gas-phase results are about 20–27 cm^{-1}. This band has also a PR type structure and can be compared with the previous fluoro and chloro analogues, which have values of 1295 and 1215 cm^{-1}, respectively. Therefore, a nice trend has been seen starting from $(NPF_2)_3$ to $(NPBr_2)_3$.

Table 1
The gas-phase observed frequencies (cm^{-1}) of $(NPX_2)_3$ where X = F, Cl and Br

Molecule	$\nu_7(E')$, in plane P—N stretching vibration (cm^{-1})	$\nu_{14}(A_2'')$, the ring deformation, out of ring plane (cm^{-1})	$\nu_{15}(A_2'')$, the P—X_2 asymmetric stretch in plane vibration (cm^{-1})
$(NPF_2)_3$	1295	980	868
$(NPCl_2)_3$	1215	625	540
$(NPBr_2)_3$	1200 (T)	560	532

(T): Tentative assignment.

These results is consistent also with the expectation and the band is shifted to lower frequency when bromine replaces the chlorine in $(NPCl_2)_3$ in order to form $(NPBr_2)_3$.

The second band observed at 560 cm^{-1} is assigned is assigned to $\nu_{14}(A_2'')$, the ring deformation out of ring plane. This band can be compared with the same mode observed in the solid $(NPBr_2)_3$ which has a value of 544 cm^{-1} [3]. The shift between the solid and the gas-phase results is about 16 cm^{-1}.

The third band at 532 cm^{-1} has been assigned to $\nu_{15}(A_2'')$, the P–Br_2 asymmetric stretch in plane vibration and the mode can be compared with the similar mode observed in the liquid form which has a value of 532 cm^{-1} [3].

The remaining bands shown in Fig. 3 are due to the starting material or to the impurities.

Semi empirical calculations for $(NPBr_2)_3$ based on the D_{3h} symmetry have been performed on $(NPBr_2)_3$ using Gamess-UK package in order to estimate the geometry of this molecule. The geometry is as follows: P–N 1.58 Å, P–Br 2.12 Å, ∠NPN 117.3°, ∠PNP 123.2° and ∠BPBr 103.2° (Scheme 1).

All the observed frequencies (cm^{-1}) of $(NPX_2)_3$ where X = F, Cl and Br determined by this gas-phase infrared spectroscopy work along the assignments are listed in Table 1.

4. Conclusion

The present work reports for the first time, the gas-phase on-line production and detection of $(NPX_2)_3$ where X = F, Cl and Br using FTIR technique. Our recorded results are consistent with the solid and liquid states of the investigated compounds which were reported earlier. Satisfactory trend was observed from fluoro to bromo analogues.

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References

[1] J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, Principles of Structure and Reactivity, fourth ed., HarperCollins College Publishers, New York, 1993.
[2] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, first ed., Pergamon Press, Oxford, 1989.
[3] T.R. Manley, D.A. Williams, Spectrochim. Acta 23A (1967) 149, and references therein.
[4] R. Stahlberg, E. Steger, Spectrochim. Acta 23A (1967) 2057.
[5] J. Emsley, J. Chem. Soc. A (1970) 109.

[6] R. Ahlrichs, S. Schunck, H. Schnöckel, Angew. Chem. 100 (1988) 418.
[7] R. Ahlrichs, S. Schunck, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 27 (1988) 421.
[8] R.M. Atkins, P.L. Timms, Spectrochim. Acta 33A (1977) 853.
[9] R. Ahlrichs, M. Bär, H.S. Plitt, H. Schnöckel, Chem. Phys. Letts. 161 (1989) 179.
[10] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., John Wiley & Sons, New York, 1986, p. 106.
[11] A.W. Allaf, Spectrochim. Acta 54A (1998) 921.
[12] I.C. Hisatsune, Spectrochim. Acta 21A (1965) 1899.
[13] T.R. Manley, D.A. Williams, Far Infrared Spectroscopy of Polymers, Preprint 467, in: Macromolecular Chemistry Symposium, Prague, August, 1965.
[14] H.J. Becher, F. Seel, Z. Anorg. Allg. Chem. 305 (1960) 148.
[15] E. Steger, R. Stahlberg, Z. Naturforsch 17b (1962) 780;
E. Steger, R. Stahlberg, Z. Anorg. Allg. Chem. 326 (1964) 243.