



# Phosphoranide production and decomposition in the gas phase



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## ARTICLE INFO

### Article history:

Received 8 February 2013

Received in revised form 20 February 2014

Accepted 20 February 2014

Available online 28 February 2014

### Keywords:

FT-ICR-MS

Reaction mechanism

Rearrangement

Energy barrier

## ABSTRACT

After characterizing the negative ion chemistry of tris(trifluoromethyl)phosphine in a previous work, new insights about the interpretation of the MS/MS mass spectrum of the phosphide anion  $(\text{CF}_3)_2\text{P}^-$   $m/z$  169 could be revealed and are described in this current work. The phosphide  $(\text{CF}_3)_2\text{P}^-$  anion,  $m/z$  169, was accelerated in a cloud of  $(\text{CF}_3)_3\text{P}$  neutrals and new product ions could be detected which do not belong to fragmentation channels. Instead, high mass anions  $m/z$  207 and  $m/z$  257 are found, and the reaction mechanism could be revealed by density functional theory (DFT) calculations at B3LYP/6-311+G(3df)//B3LYP/6-31+G(2d) level of theory. The formation of the phosphoranide  $(\text{CF}_3)_3\text{PF}^-$   $m/z$  257 is the result of a fluoride anion transfer from the accelerated phosphide anion  $(\text{CF}_3)_2\text{P}^-$   $m/z$  169 to the  $(\text{CF}_3)_3\text{P}$  neutral  $m=238$ . Decomposition of the newly formed phosphoranide  $(\text{CF}_3)_3\text{PF}^-$   $m/z$  257 leads to the formation of smaller phosphoranides  $(\text{CF}_3)_2\text{PF}_2^-$   $m/z$  207 and  $\text{CF}_3\text{PF}_3^-$   $m/z$  157 as a result of successive  $\text{CF}_2$  eliminations. A new rearrangement in the formed phosphoranide  $(\text{CF}_3)_2\text{PF}_2^-$  could be revealed, whereby a C–C bond formation can take place and the product anion  $\text{C}_2\text{F}_5^-$   $m/z$  119 could be experimentally obtained.

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## 1. Introduction

Tetrakis(trifluoromethyl)phosphoranide  $(\text{CF}_3)_4\text{P}^-$  can serve as an efficient trifluoromethylating agent, which adds  $\text{CF}_3$  group to specific substrates in fluorine chemistry. However, the stability of this phosphoranide was questioned by several authors in the past [1] and we previously confirmed that the  $(\text{CF}_3)_4\text{P}^-$  anion could not be obtained as a stable product anion in the gas phase, when the  $\text{CF}_3^-$  ion was let to react with  $(\text{CF}_3)_3\text{P}$  neutral within the scope of a gas phase ion-molecule reaction under ICR conditions. Kanawati et al. [2] provided a mechanism for this reaction and could explain, by DFT calculations, why  $(\text{CF}_3)_3\text{PF}^-$  was formed as the highest mass anion instead of the product anion  $(\text{CF}_3)_4\text{P}^-$  in the gas phase and under ion cyclotron resonance (ICR) conditions. In their previous study, the authors showed that when  $\text{CF}_3^-$  nucleophile approaches the phosphorous center in  $(\text{CF}_3)_3\text{P}$ , the fluoro-substituent of the  $\text{CF}_3^-$  nucleophile attacks the phosphorous center in  $(\text{CF}_3)_3\text{P}$  instead of having a C–P attack. When one of the three fluorines in the  $\text{CF}_3^-$  attacks  $(\text{CF}_3)_3\text{P}$ , a difluorocarbene can be eliminated to produce the phosphoranide  $(\text{CF}_3)_3\text{PF}^-$ .

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In this paper, we shed the light on the possibility of the obtained phosphoranide  $(\text{CF}_3)_3\text{PF}^-$  to undergo several successive  $\text{CF}_2$  eliminations to produce other new phosphoranides with smaller masses. The mechanism for these successive  $\text{CF}_2$  eliminations were revealed as their corresponding transition state geometries could be obtained by reliable DFT calculations. This fact reflects the low stability of the phosphoranide  $(\text{CF}_3)_3\text{PF}^-$  and questions its deployment as a trifluoromethylating agent, especially when  $\text{CF}_3\text{-SiMe}_3$  exists for this purpose [3–5]. The gas phase ion chemistry of  $\text{CF}_3\text{-SiMe}_3$  trifluoromethylation reagent was investigated in the gas phase under FT-ICR conditions [6]. Kolomeitsev et al. described advances in trifluoromethylating phosphorous compounds [7]. In solution, the phosphoranides  $(\text{CF}_3)_4\text{P}^-$  and  $(\text{CF}_3)_3\text{PF}^-$  are only stable when large cations such as tetramethylammonium or  $\text{K}^+$  18-crown-6 ether cations are used as stabilizing counter ions [1].

A mechanism for a new possible rearrangement in the phosphoranide anion  $(\text{CF}_3)_2\text{PF}_2^-$  to produce the anion  $\text{C}_2\text{F}_5^-$  with a direct C–C bond formation is also explained in this work. We show that this rearrangement which leads to direct C–C bond formation can only occur in  $(\text{CF}_3)_2\text{PF}_2^-$ . The driving force for this rearrangement is the elimination of a very stable  $\text{PF}_3$  neutral.

We also shed the light in this work on a new route for the formation of the phosphoranide anion  $(\text{CF}_3)_3\text{PF}^-$   $m/z$  257 as a result of the reaction of the accelerated phosphide anion  $(\text{CF}_3)_2\text{P}^-$   $m/z$  169 with  $(\text{CF}_3)_3\text{P}$  neutrals. We show that the phosphide anion is a good

fluoride anion donor and can produce the phosphoranide  $(\text{CF}_3)_3\text{PF}^-$   $m/z$  257 by a fluoride anion transfer to the  $(\text{CF}_3)_3\text{P}$  phosphine.

Characterization of negative ions in mass spectrometers is not widely common when compared to the investigated positive ions gas phase chemistry. However, several authors could succeed in giving deep details about the chemistry of negative ions in the gas phase and their behavior under different conditions depending on the mass analyzers they use. DePuy et al. [8] described chemical reactions of anions in a flowing afterglow apparatus. A main review about fragmentation of several classes of organic negative ions exists [9]. Several reviews about negative chemical ionization of organic molecules exist [10–13]. Computational chemistry plays an important role in most mass spectrometric investigations because it enables to explain proposed mechanisms of observed fragmentation pathways. Alcamí et al. [14] explained the usefulness of computational methods and showed that these are even mandatory tools in some cases to explain interesting ion behavior in the gas phase. Kanawati et al. studied many gas phase rearrangements of negative ions of mono- di- as well as oxocarboxylic acids by running CID experiments and calculating energy profiles for observed fragmentation channels [15–18]. Stereochemical differences in negative ion fragmentation of ascorbic acid glycosidic isomers could also be achieved by Kanawati et al. in a combined experimental and theoretical investigation [19]. It should be mentioned that very little is known about the chemistry of phosphoranides, especially in the gas phase. A review for the known solution chemistry of phosphoranides is given in the literature [20].

## 2. Calculations

The electronic structure calculations were performed on a stand-alone computer using Density Functional Theory, incorporated in Gaussian 03W program [21]. All geometry optimizations were performed using 6-31+G(2d) basis set. Frequency calculations were also done for each optimized geometry using the same basis set 6-31+G(2d) to obtain the zero point vibrational energy (ZPVE). This value is multiplied by the scaling factor 0.9804 to correct for vibrational anharmonicities [22]. Single point energy (SPE) calculations were done using 6-311+G(3df) level of theory. The use of diffuse functions was important to represent the correct geometry of anionic species [23]. The discussed reactions are described in the form of energy changes  $\Delta E$  instead of  $\Delta G$ . This is because considering Gibbs free energies will contribute to larger errors in the calculated energy barriers (because of the term  $T\Delta S$ , which is not accurately defined under ultra high vacuum inside ICR cells). Stability tests on all calculated structures were performed to ensure that the used wave function does represent the lowest energy solution of the self consistent field (SCF) equations. All studied closed shell molecules and anions were calculated as singlets (the most stable electronic form).

For geometry optimization, the analytical gradient optimization routines [24] were used in combination with the GDIIS algorithm [25–27]. The requested convergence in the density matrix was  $10^{-8}$ , the threshold value for maximum displacement was 0.0018 Å, and that for the maximum force was 0.00045 Hartree/Bohr. The nature of the stationary points was established by calculating and diagonalizing the Hessian matrix (force constant matrix). Transition structures were characterized through normal-mode analysis (frequency analysis). The transition vector associated with the unique imaginary frequency has been determined in each found transition state and is provided as animation in Supplementary material. This vector represents the eigenvector associated with the unique negative eigenvalue of the force constant matrix, which indicates that the found structure corresponds to a first order

saddle point (transition state). In order to further check that the found transition state actually connects two energy minima structures with each other (reactant with product), intrinsic reaction coordinate (IRC) calculations [28] in all found transition state geometries, were performed in mass-weighted internal coordinates [29]. All geometries of electronic structures calculated were viewed by GaussView program [30]. Mechanistic studies for isodesmic transformations (gas phase intramolecular rearrangements and ion fragmentation processes) are presented in this paper.

## 3. Results and discussion

Tris(trifluoromethyl)phosphine  $(\text{CF}_3)_3\text{P}$  yields only one major negative ion species, the phosphide ion  $(\text{CF}_3)_2\text{P}^-$  ( $m/z = 169$ ) by dissociative thermal electron attachment (negative mode ionization by the use of an electron source rhenium hot cathode). When the phosphide anion  $(\text{CF}_3)_2\text{P}^-$  is accelerated inside an ICR cell by applying single shot radial ion excitation pulse (in resonance with the cyclotron frequency of the trapped phosphide anion in the cylindrical ICR cell) in a cloud of  $(\text{CF}_3)_3\text{P}$  neutrals for 1 s reaction time, new product ions (phosphoranides) with masses higher than the phosphide itself could be observed in the self CID of the phosphide anion (Fig. 1).

### 3.1. Formation of the phosphoranide $(\text{CF}_3)_3\text{PF}^-$ , $m/z$ 257

Fig. 1 summarizes the outcome of the reaction between the accelerated phosphide anion  $(\text{CF}_3)_2\text{P}^-$  anion and  $(\text{CF}_3)_3\text{P}$  neutrals. High resolution FT-ICR-MS measurements performed in a previous study as well as CID experiments for the three high mass major product ions  $m/z$  257, 207 and 157 confirmed their identities as the phosphoranides  $(\text{CF}_3)_3\text{PF}^-$ ,  $(\text{CF}_3)_2\text{PF}_2^-$  and  $\text{CF}_3\text{PF}_3^-$ , respectively. The reaction time was 1 s at a relatively high pressure of  $2 \times 10^{-7}$  mbar. It should be mentioned that the phosphide anion  $(\text{CF}_3)_2\text{P}^-$  is hardly accessible in solution chemistry and could also be isolated for X-ray analysis by its successful stabilization through coordination to Pentacarbonyl Tungsten with 18-crown-6-K as a counter ion [31].

Fig. 2 shows the optimized calculated geometry of the transition state which could be identified to illustrate how the ion-molecule reaction in Eq. (1)- Scheme 1 between the accelerated phosphide anion  $(\text{CF}_3)_2\text{P}^-$   $m/z$  169 and the neutral phosphine  $(\text{CF}_3)_3\text{P}$  can take place. The vibration of the fluoride anion, which is marked by a star, is given in the form of an animation in Supplementary material and this vibration builds the intrinsic reaction coordinate for the fluoride anion transfer. The optimized geometry of the transition

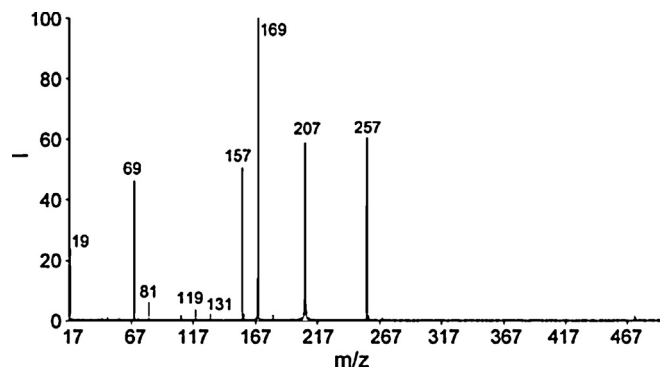


Fig. 1. Accelerated ion-molecule reaction between the radially accelerated phosphide ion  $(\text{CF}_3)_2\text{P}^-$   $m/z$  169 and the phosphine neutrals  $(\text{CF}_3)_3\text{P}$  inside the ICR cell. Reaction time is 1 s at  $2 \times 10^{-7}$  mbar.

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