4. This question is about the analysis of a flame-retardant

Retardol C, Pyroset TKC and Proban CC are three trade names given to a flame-retardant used to produce crease-resistant and flame-retardant finishes on textiles such as those used to make nightclothes for children.

The flame-retardant is a salt , $X^+ Y^-$, prepared by the reaction between phosphine, PH_3, and methanal in dilute aqueous acid. The anion Y^- simply depends on which acid was used in the preparation.

(a) Draw the structures of phosphine and methanal, clearly indicating the geometry of each molecule.

The mass spectrum of X^+ (down to 50 *m/z*) is shown over the page, together with the proton and phosphorus-31 NMR spectra. The carbon-13 NMR spectrum of X^+ (not shown) shows there is just one environment of carbon atom in the cation.

(b) By inspection of the ^1H NMR spectrum, suggest the number of environments of hydrogen atoms in X^+. What is the ratio of the number of hydrogen atoms in the different environments?

When the sample is mixed with a little D_2O instead of H_2O, the signal at 6.25 ppm in the ^1H NMR spectrum disappears.

(c) What functional group does this suggest may be present in X^+?

The ^{31}P NMR spectrum shows one signal split into a multiplet due to coupling to hydrogens.

(d) How many hydrogen nuclei is the phosphorus coupling to?

The mass spectrum shows the molecular ion and a number of fragmentation peaks.

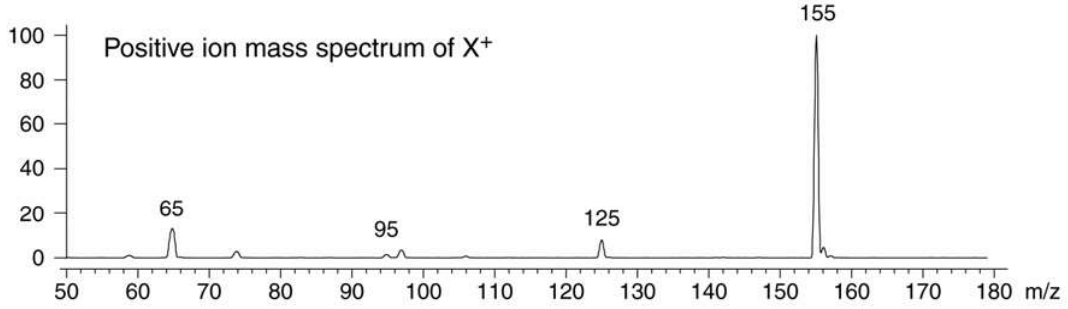
(e) **i)** The fragmentation process shows consecutive losses of a 30 mass unit. Suggest the formula for the fragment lost.

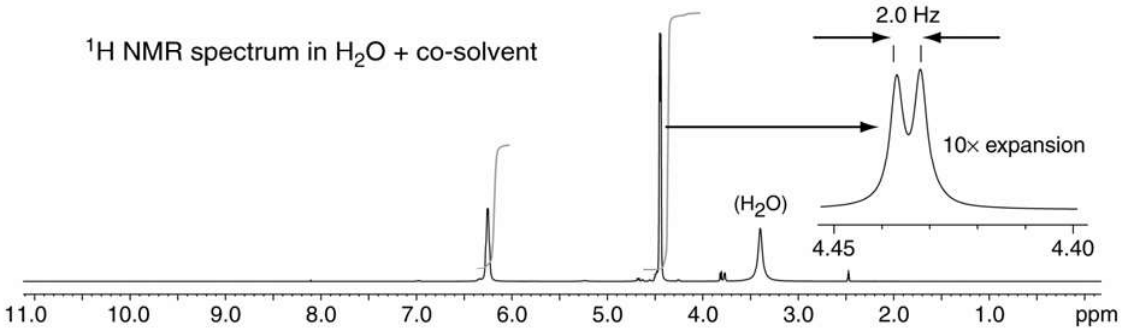
ii) Suggest a formula for the X^+ ion.

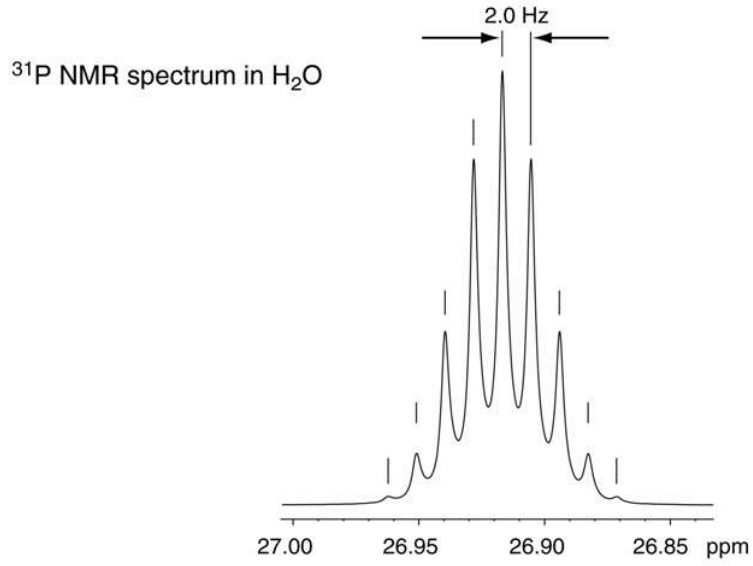
iii) A mass spectrum of the D_2O solution of X^+ no longer shows a peak at 155, but instead shows a peak at a higher *m/z*. At what value of *m/z* would you expect this new peak to come?

(f) **i)** Suggest a structure for the cation X^+, clearly indicating its geometry.

ii) Suggest a structure for the ion at *m/z* = 65.


Positive ion mass spectrum of X+
155
65
95
125
100
80
60
40
20
0
50 60 70 80 90 100 110 120 130 140 150 160 170 180 m/z


1H NMR spectrum in H2O + co-solvent
2.0 Hz
10× expansion
(H2O)
4.45
4.40
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 ppm


31P NMR spectrum in H2O
2.0 Hz
27.00 26.95 26.90 26.85 ppm