



Bomb Calorimetric Study of a Series of Energetic Linear Polyphosphazenes

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Abstract: Energetic linear polyphosphazenes are of potential interest as novel binders for energetic formulations. However, the presence of phosphorus in these materials renders their combustion chemistry significantly different to that of conventional binders. This paper explores the combustion chemistry of a series of energetic polyphosphazenes. The heat of combustion of each member of the series has been measured by bomb calorimetry, and the water-soluble combustion products have been identified and quantified using NMR Spectroscopy and Ion Chromatography. Since some of the combustion products are hydrolytically unstable, it was necessary to stabilise the initial combustion product mixtures by using a buffer solution instead of pure water in the bomb, and then to determine the composition of the stabilized product mixtures in order to obtain meaningful values for the heats of combustion and thence heats of formation. The thermochemical measurements themselves were made with pure water in the bomb. The composition and structures of the various polyphosphazenes have been correlated with their heats of combustion and should enable polyphosphazenes with specific thermochemical properties to be identified. The ‘combustion’ of the polyphosphazenes under a nitrogen atmosphere has also been studied.

Keywords: energetic polyphosphazenes, heat of combustion, heat of formation

Introduction

Energetic polyphosphazenes have been suggested as promising, low hazard binders with enhanced energy-density [1]. The oxygen combustion chemistry of five such energetic, linear polyphosphazenes, the random unit structures of which are shown in Figure 1, has been studied. The values of the measured internal energy of combustion (ΔU_c) were employed to calculate the standard enthalpies of combustion (ΔH_c°) and thence the enthalpies of formation (ΔH_f°) of the polymers, which are necessary for the semi-empirical estimation of the enthalpies of detonation.

Results and discussion

Preparation and structure elucidation

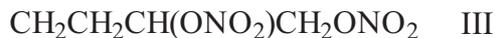
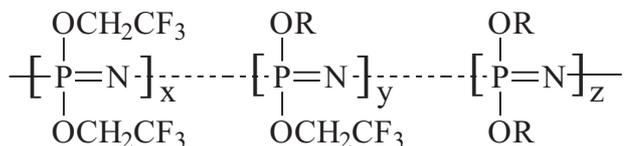


Figure 1. Random structures of five energetic, linear polyphosphazenes.

Polymers I, II, III, IV and V (Figure 1) were prepared by reacting an appropriate alkoxide with linear poly[bis(2,2,2-trifluoroethoxy)phosphazene] to generate a random, mixed substituent polymer, and then nitrating the initial

substitution product [1]. The degrees of trifluoroethoxy group replacement in the final polymers was estimated by ^1H NMR spectroscopy and CHN elemental analysis, and were found to range between 31% and 76% depending on the size of the nucleophile reacted with the homopolymer (Table 1), and the reaction time. [100% energetic substituent (%ES 100) represents complete replacement of both trifluoroethoxy groups in the substitution reaction.] The empirical formulae of each energetic polymer were derived from the values of the percent of energetic substituent.

Table 1. Percent energetic substituent as estimated by ^1H NMR spectroscopy and CHN elemental analysis

Resultant energetic polyphosphazene	Polymer	Energetic substituent (% by ^1H NMR)	Energetic substituent (% by CHN elemental analysis)
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.48}(\text{OCH}_2\text{CH}_2\text{ONO}_2)_{1.52}]$	I (single batch)	76	74
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{1.38}(\text{OCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{0.62}]$	II batch 3	31	-
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.70}(\text{OCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.30}]$	II batch 1	65	-
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.60}(\text{OCH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.40}]$	II batch 2	70	69
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.82}(\text{OCH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.18}]$	III batch 1	59	-
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.68}(\text{OCH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.32}]$	III batch 2	61	62
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.66}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.34}]$	IV batch 1	67	67
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{1.00}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.00}]$	V batch 1	50	-
$[\text{NP}(\text{OCH}_2\text{CF}_3)_{0.98}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2)_{1.02}]$	V batch 2	51	54

Approximate oxygen balance values for the highest substituted specimens of each polymer were estimated assuming ideal combustion behaviour *viz.* assuming only N_2 , CO_2 , H_2O , HF and H_3PO_4 are formed (Table 2). All five polymers are oxygen-deficient, with polymer II exhibiting the least negative oxygen balance. Most of the polymers are, however, less oxygen-deficient than the carbon-based energetic polymers polyGLYN, polyNIMMO and GAP, as shown in Table 2.

Table 2. Values of the oxygen balance (%) of five energetic polyphosphazene-based polymers and of three carbon-based polymers

Energetic polymer (% energetic substituent by ¹ H NMR)	Unit empirical formula	Oxygen balance
I (76%)	C _{4.00} H _{7.04} O _{6.56} N _{2.52} F _{1.44} P _{1.00}	-42.5
II (70%)	C _{5.40} H _{8.20} O _{10.40} N _{3.80} F _{1.80} P _{1.00}	-27.3
III (61%)	C _{6.44} H _{10.10} O _{9.32} N _{3.44} F _{2.34} P _{1.00}	-44.1
IV (67%)	C _{8.02} H _{13.38} O _{10.04} N _{3.68} F _{1.98} P _{1.00}	-58.1
V (51%)	C _{8.08} H _{13.18} O _{8.12} N _{3.04} F _{2.94} P _{1.00}	-67.8
PolyGLYN	C _{3.00} H _{5.00} O _{4.00} N _{1.00}	-60.5
PolyNIMMO	C _{5.00} H _{9.00} O _{4.00} N _{1.00}	-114.3
GAP	C _{3.00} H _{5.00} O _{1.00} N _{3.00}	-121.2

Combustion chemistry studies

Samples (~300 mg) of each energetic polymer were combusted in oxygen at 30 atm pressure in a Gallenkamp ‘Autobomb 305’ static, adiabatic, oxygen bomb calorimeter, using a Parr 1108-Cl halogen-resistant bomb. The calorimeter was calibrated with benzoic acid thermochemical standard (Parr Inc.). A measured volume of either pure water (thermochemical measurements) or pH 7 buffer (imidazole-imidazolium oxalate 0.8 M; used to stabilise the hydrolytically unstable products for product analysis) was added to the bomb before firing. The combustion products, other than CO₂, N₂ and H₂O, arising from all samples were identified by ¹⁹F NMR spectroscopy (Figure 2) and ion exchange chromatography (Figure 3) as *nitric acid, hydrogen fluoride, orthophosphoric acid, monofluoro- and difluoro-phosphoric acids*. There is no evidence for the formation of polycondensed phosphorus acid species [2], their fluorinated analogues [3], and carbon-based fluorinated gases [4, 5] (*e.g.* CF₄, C₂F₆); hexafluorophosphoric acid is only formed when energetic polyphosphazenes with low %ES values, and the precursor linear poly[bis(2,2,2-trifluoroethoxy)phosphazene], are burned. The hydrolytic instability of monofluoro- and difluoro-phosphoric acid in unbuffered solution, which has been investigated by ¹⁹F and ³¹P NMR spectroscopy by other workers [6-8], was confirmed by ¹⁹F NMR spectroscopy. The use of ¹⁹F NMR spectroscopy is preferred over ³¹P NMR spectroscopy for the analysis of these systems due to the simpler spectra in the case of the former [3, 9].

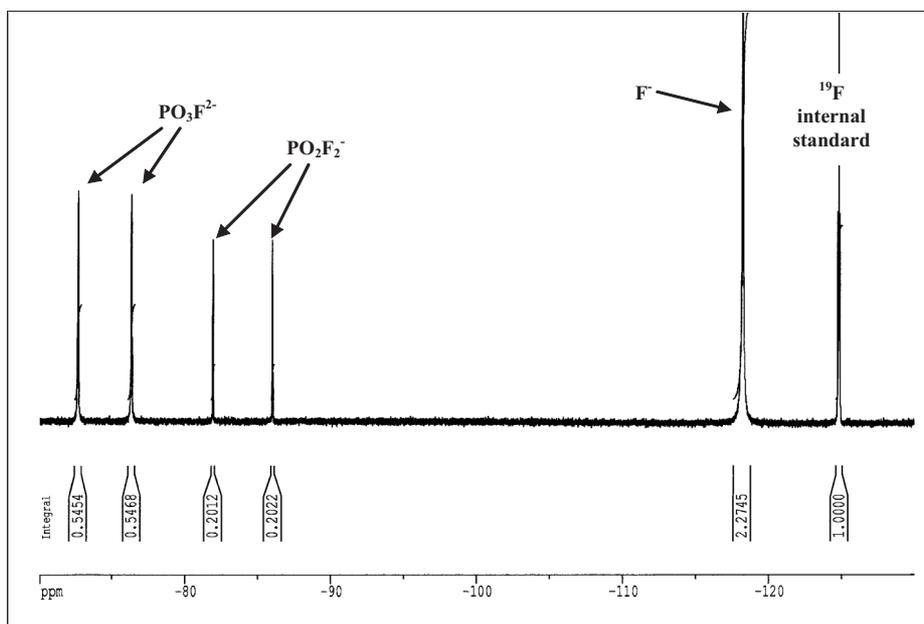


Figure 2. Typical ^{19}F NMR spectrum (acetone- d_6 internal probe) of the undiluted, buffered bomb solution.

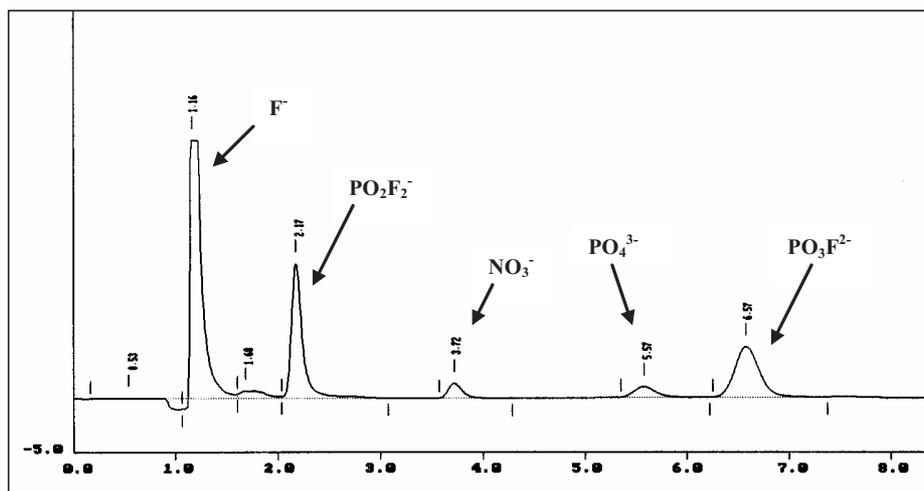


Figure 3. Typical ion chromatogram (eluent: aqueous $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$, 18/17 mM, pH 10.3; retention time in minutes) of the diluted, buffered bomb solution.

The chemical analysis of the combustion products indicates that the overall combustion process of the polymers in excess oxygen follows the stoichiometry shown in Equation 1, which assumes that no polycondensed phosphorus acids and their fluorinated analogues are formed.

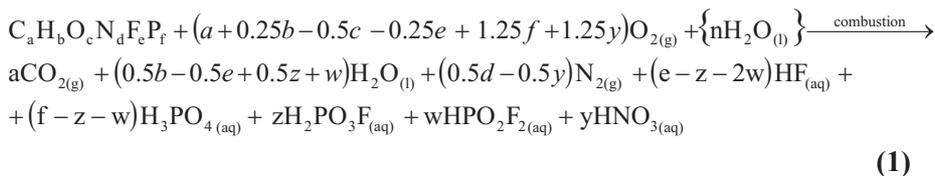


Table 3. Measured values of the internal energy of combustion (ΔU_c) for polymers I-V with different percent energetic substituent

Energetic Polymer	%ES*	ΔU_c (J g ⁻¹)
I	76	-10520 ± 180 [1.7%]
	31**	-8880 ± 140 [1.6%]
II	65	-8640 ± 105 [1.2%]
	70	-9220 ± 160 [1.7%]
III	59	-10890 ± 160 [1.5%]
	61	-11250 ± 100 [0.9%]
IV	67	-13060 ± 210 [1.6%]
V	50	-13910 ± 520 [3.7%]
	51	-14450 ± 180 [1.2%]

* %ES = percent energetic substituent (as measured by ¹H NMR spectroscopy).

** Some hexafluorophosphoric acid is formed on combustion.

Table 3 summarises the internal energy of combustion (ΔU_c) of different batches of the five energetic polymers, with different percent energetic substituent. Thermochemical corrections were subsequently made to account for the amounts of orthophosphoric acid [10], nitric acid [11], monofluoro- and difluoro-phosphoric acids [12], [and hexafluorophosphoric acid when present], formed in the bomb, while the ‘Washburn corrections [13] to standard states’ were neglected.

As expected, the measured values of the internal energy of combustion were found to be dependant upon the percent energetic substituent in the polymer. Polymer V showed the highest calorific value, despite having a lower percent energetic substituent than any of the other polymers. By converting the experimentally derived ΔU_c values into ΔH°_c values [14] and direct subtraction of the latter quantities from the sum of the standard enthalpies of formation of

the combustion products [12, 15, 16] it was possible to calculate the values of the standard enthalpy of formation ($\Delta H^\circ_{f(298)}$) of each energetic polymer at different %ES values (Table 4). Unfortunately however the percentage error in the ΔH°_f values is high ($< \pm 5\%$). This is because the absolute error in the ΔH°_f values is essentially the same as that in the ΔH°_c values, there being relatively small errors in the ΔH°_f values of the combustion products. The ultimate goal of the project will involve graphical correlation of ΔH°_f and hence ΔH°_{det} with %ES for each polymer, and should enable energetic polyphosphazenes with specific thermochemical properties to be identified.

Table 4. Standard enthalpy of combustion (ΔH°_c) and standard enthalpy of formation (ΔH°_f) of energetic polymers I-V

Energetic polymer	%ES*	ΔH°_c [J g ⁻¹]	ΔH°_c [kJ mol ⁻¹]	ΔH°_f [J g ⁻¹]	ΔH°_f [kJ mol ⁻¹]
I	76	-10530 ± 180	-2672 ± 46	-5849 ± 180	-1484 ± 46
II	31**	-8870 ± 140	-2610 ± 41	-7277 ± 140	-2141 ± 41
	70	-9209 ± 160	-3296 ± 57	-4610 ± 160	-1650 ± 57
III	61	-11250 ± 100	-4052 ± 36	-4627 ± 100	-1667 ± 36
IV	67	-13040 ± 210	-4821 ± 82	-5213 ± 210	-1927 ± 82
V	51	-14460 ± 180	-5345 ± 66	-4282 ± 180	-1583 ± 66
PolyGLYN				-2710***	-323***
PolyNIMMO				-2290***	-337***
GAP				-1150***	-114***

* %ES = percent energetic substituent (as measured by ¹H NMR spectroscopy).

** Some hexafluorophosphoric acid is formed on combustion.

*** Reference [14].

A further step towards estimating the ΔH°_{det} of the energetic linear polyphosphazenes was made by initiating 'combustion' of polymer II (%ES 64) in an atmosphere of nitrogen (30 atm). In these experiments the products were not greatly different from when II was combusted in an oxygen atmosphere, except that HPF₆ and CF₃CH₂OH (the latter is normally observed when the polyphosphazenes are pyrolysed) were also present. The accountancy for F and for P in the combustion products was > 80%. The residue amounted to 4.0-6.4 wt%. These results suggest that in the absence of external oxygen, the preferred processes are conversion of F and P to HF, P₂O₅ (H₃PO₄) and fluorinated analogues. Any surplus oxygen is then expected to be distributed between the

oxidation of C and the remaining H in the normal manner. The ΔU_c value was $3510 \pm 200 \text{ J g}^{-1}$, compared to $8960 \pm 260 \text{ J g}^{-1}$ for combustion of the same batch in oxygen.

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