A study of fire-retardant mechanisms in the gas phase by FTIR spectroscopy

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Abstract: **This paper presents initial results of vapour-phase chemistry of volatile fire retardants, which may contain phosphorus, bromine or iron, in the presence of fuel from the burning material. Two studies have been carried out using an isothermal tubular-flow reactor. In the first study the influence of a flame-retardant ignition limits of fuel/fire-retardant additive at different temperatures has been determined. These results indicate that a commercial fire retardant (Reofos® 95), a phosphorus-containing additive, and ferrocene, are effective gas-phase additives with isooctane, but that bromobenzene is not. With toluene, all additives have a negative effect on the ignition temperature of the fuel. In the second study, the gas-phase mechanisms of fire-retardant action have been studied using Fourier-transform infrared spectroscopy (FTIR). The FTIR study combined with target factor analysis chemometric software indicates that product and intermediate gas-phase species (H_3PO_4, $(CH_3O)_2P(OH)O$ and $CH_3OP(OH)_2O$) can be detected over a wide range of temperatures (400–900 °C). © 2000 Society of Chemical Industry**

INTRODUCTION

An understanding of the mechanism of action of fire-retardant additives during combustion is very important to the development of our understanding of fire hazards. Fire retardants usually act in the condensed phase, for example by char promotion through dehydration, or fire retardants may act in the vapour phase. While there is general agreement on the likely mechanisms of action for some well-known fire retardants, there is little published on the detailed mechanisms. Green[1] in his review of phosphorus-containing flame retardants, stated that phosphorus can be found in all phases. Organophosphorus fire retardants such as triaryl phosphates and dimethyl methylphosphonate (DMMP) are widely used as flame retardants in, for example, polycarbonate/ABS blends, fire-retardant hydraulic fluids and lubricants.[2] They are normally considered to act in the condensed phase, but the possibility that some degree of vapour-phase activity may be occurring in view of the relative volatility of some of these additives[3] needs to be considered. The mechanism involved in the vapour phase is unclear, but Twarowski[4] has suggested that phosphoric acid, formed during gas-phase combustion, acts as a catalytic radical-scavenging agent.

In a later review, Green[5] also looked at halogenated compounds; these function in the vapour phase by radical mechanisms. Brominated organic compounds are widely used as fire retardants;[6–9] these are also considered to act as free radical scavengers in the vapour phase and although there is currently much activity in the search for halogen-free additives,[9,10] they are still widely used.

Ferrocene has been studied both as a potential smoke suppressant and as a flame retardant.[11–14] Because of its volatility and relative thermal stability, ferrocene may act, to some degree, in the vapour phase. Troitzsch[15] in his work with ferrocene indicated a gas-phase mechanism, and Frazee and Anderson[16] have also suggested this. Others,[13,14,16,17] however, suggest there is strong evidence that ferrocene acts via a condensed-phase mechanism.

The interactions between combustible materials and fire-retardant additives will be complex, and will also depend on factors such as the presence of other additives and the actual fire conditions such as ventilation. We report here initial studies on the vapour-phase chemistry of several volatile fire-retardant (FR) model compounds. Two separate experiments were conducted, both employing the novel use of a pre-heater to volatilize the liquid fuels/fire-retardant additive mixtures and to pre-heat the gaseous components used to the same temperature, enabling good control of the reaction stoichiometry. The first experiment was designed to determine the influence of FR additives and stoichiometry on

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ignition temperatures, and the second experiment was designed to study the gas-phase chemistry close to ignition using FTIR spectroscopy together with CO and CO_2 analysis with subsequent processing of the data using chemometric software.[18] The fuels used were toluene and 2,2,4-trimethylpentane (iso-octane) as representative model compounds for the pyrolysis products from aromatic and aliphatic polymers, respectively.

Kong et al[19] used a 1 litre ignition bomb to measure ignition temperatures of fire retardants, and found that this method ensured accurate control of the composition of the gas mixture, which was not possible with common standard test methods. Liao et al[20] measured flammability limits using a tubular flame, and stated that this method is superior to the explosion method,[21] Ciajolo et al[22] studied the slow combustion of iso-octane and toluene/n-heptane mixtures with a jet-stirred flow reactor where they found that iso-octane tended to form an oxygenated fuel-skeleton retaining species which was responsible for the reactivity and autoignition of the fuel. Emdee et al[23] studied the initial chemistry of toluene oxidation, and Bittker[24] used a flow reactor and ignition delay times to develop a toluene oxidation model.

A standard test method for autoignition of liquid chemicals is the ASTM method E-659–78,[25] which uses an electrically-heated crucible furnace. This apparatus is capable of being used for the study of solids and liquids but is unsuitable for the study of gases. Published data for minimum ignition temperatures using hot-surface ignition experiments vary by up to 500 °C depending on test conditions.[19]

Kallonen[26] states that there are many advantages to FTIR as a technique for studying combustion gases; they include high resolution and simultaneous measurement over a wide range of wavelengths. Paul[27] also found that the use of FTIR enabled determination of a number of fire gases simultaneously and that on-line analysis allowed the fire path to be followed. Su et al[28] used FTIR to study halons during fire-suppression tests, and Kim et al[29] found that the evolved gaseous product results quantified by FTIR compared well with those in the literature.

EXPERIMENTAL
Ignition point study
Figure 1 shows a schematic diagram of the tube furnace and the pre-heater system used in the ignition point study. The system consisted of a motorized syringe containing the liquid fuel and fire retardant which had been pre-mixed. The fuel mix was injected into the furnace using a Razel A-99 syringe pump, calibrated using 20 ml syringes, to deliver a steady, selectable flow rate. The fuel mix was pre-heated to above its boiling temperature before it reached the furnace, by heating the fuel line with a two-stage power supply consisting of a Variac and a 3 A, 240–40 V step-down transformer.
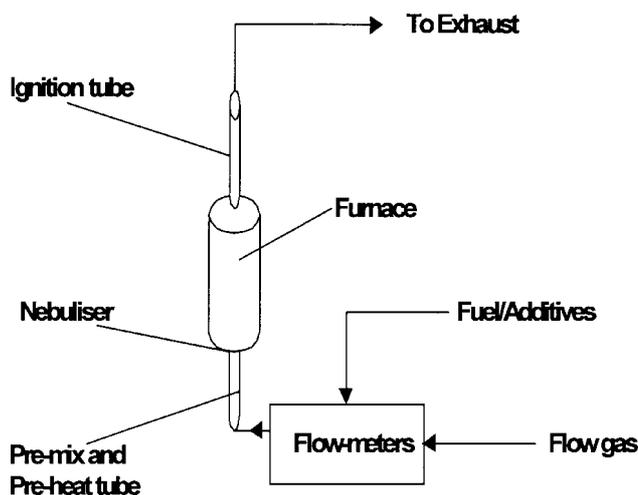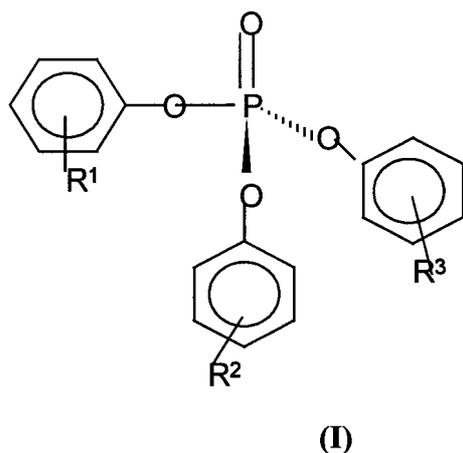

Figure 1. Ignition point apparatus.

Air supplied by an oil-free compressor, and controlled with an in-line flow meter, entered the pre-mix tube and was heated to above the boiling temperature of the liquid fuel-mix by contact with the fuel line, which passed through the pre-mix tube. At the top of the pre-mix tube the hot air and fuel were mixed in the nebulizer and entered the quartz reaction tube, which had an inner diameter (id) of 20 mm and a length of 480 mm. The quartz reaction tube passed through a vertical, single-phase tube furnace, which had an id of 40 mm and was 350 mm long. The temperature was measured by a K Type thermocouple supplied by Omega Engineering Ltd, which was suspended down the centre of the reaction tube. The thermocouple gave a maximum error in temperature of ± 1%.

At the start of the experiment, air was pumped into the pre-heater at 31min^{-1} controlled by a GAP three-line flow meter. The air was heated at temperatures up to 500 °C with the heated fuel line. The fuel pump was then started at a pre-set rate in the range $0–2.0 \text{ml s}^{-1}$, after which the heated fuel and air were mixed at the nebulizer and passed into the flow reactor. The furnace temperature was then raised until ignition of the fuel mix occurred. Upon ignition, the fuel was switched off and the furnace was allowed to cool to more than 50 °C below the ignition point. The fuel flow was then restarted and the furnace temperature raised again until ignition occurred a second time.

This process was repeated at different fuel rates corresponding to a local equivalence ratio (LER) in the range 0.1–2.5, to obtain a profile of ignition temperatures against.

Initially additive-free iso-octane or toluene fuel was studied, then fire-retardant additives; bromobenzene 5–25% (v/v), Reofos®95 5–25% (v/v), (all in 5% increments) and ferrocene 1–2% (w/v), (1% increment), were added to each fuel. The Reofos® additives are a homologous series of triarylphosphates

with the general structure (**I**).

(I)

FTIR study

Figure 2 shows a block flow diagram of the FTIR apparatus which consisted of the same syringe and pre-heater/pre-mix system as used in the ignition point study. The air and carrier gas, controlled with in-line flow meters, entered the pre-mix tube and were heated to above the boiling temperature of the liquid fuel before meeting the gaseous fuel mix at the nebulizer. The quartz reaction tube, id 20 mm and length 480 mm, passed through a horizontal three-zone Carbolite TZF12 tube furnace, with an overall length of 500 mm and a maximum id of 56 mm.

Both liquid and gaseous fuels could be introduced by direct injection into the reaction zone via the stainless steel fuel line as described above. The reacted gases passed out of the furnace via a heated (200 °C) stainless steel gas line and through an in-line (Whatman No 1) filter. This heated gas line entered the Perkin-Elmer 1710 FTIR instrument via the sample compartment, containing a heated gas cell, kept at a temperature of 185 °C, with a pathlength of 100 mm. The gas then passed through a series of gas monitors. Carbon dioxide was measured by an Analytical Development Corporation PM3 series monitor and the carbon monoxide levels were measured by an
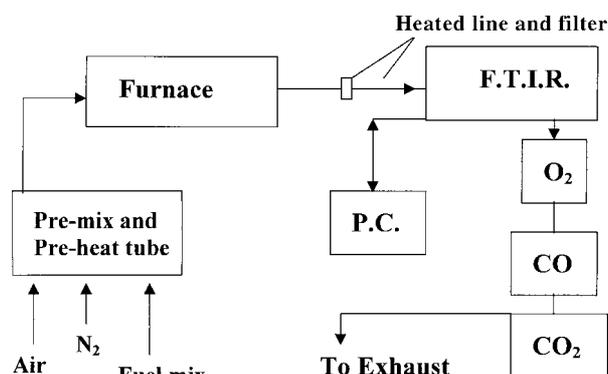
Analytical Development Corporation CO monitor. Oxygen concentrations were measured using a Servomex OA250 multi-range paramagnetic oxygen analyser.

In this study, air at $1 \, l\,min^{-1}$ and nitrogen at $5 \, l\,min^{-1}$ were pumped into the pre-heater, controlled by the GAP three-line flow meter. Ventilation conditions could be varied by adjusting the air-to-nitrogen ratio and/or by adjusting the fuel flow. For iso-octane, LERs of $\phi = 0.5$ and $\phi = 1.0$ were studied at constant total gas flow, and ϕ was varied by adjusting the fuel flow within the temperature range 400–950 °C. Trimethyl phosphate (TMP) as a simple model for phosphorus-based fire retardants and the commercial fire retardant Reofos® 95 were studied, and were added at a concentration of 5% (v/v). The additives were dissolved in the fuel before use. Measurements were carried out at atmospheric pressure.

All equipment was allowed to stabilize at the set temperature for 30 min. Twenty FTIR scans were acquired at a spectral resolution of $4 \, cm^{-1}$ and a scan time of 20 s, and the spectra were averaged and stored for each run.

Chemicals

The fuels used in these studies were toluene (BDH) and 2,2,4-trimethylpentane (Aldrich), both of GPR purity. Air and oxygen-free nitrogen were supplied by BOC Ltd. Bromobenzene, ferrocene and trimethylphosphate (TMP) were supplied by Aldrich. Reofos® 95 was supplied by FMC Ltd.

RESULTS
Ignition temperature study

In Fig 3 the ignition temperatures are shown as a function of temperature and LER for iso-octane, iso-octane plus bromobenzene (5% v/v), ferrocene (1% w/v) and Reofos® 95 (5% v/v) in the vapour phase. Bromobenzene actually reduced the ignition tempera-
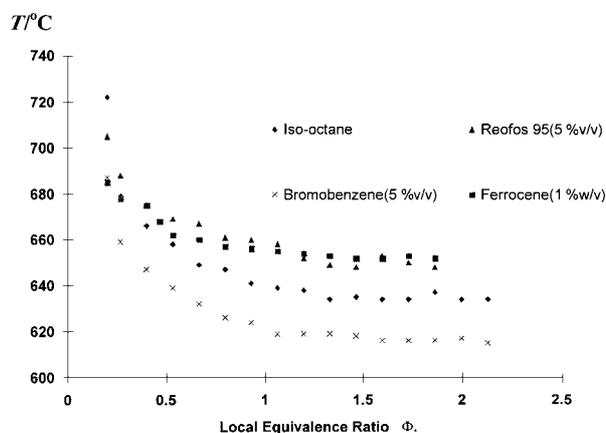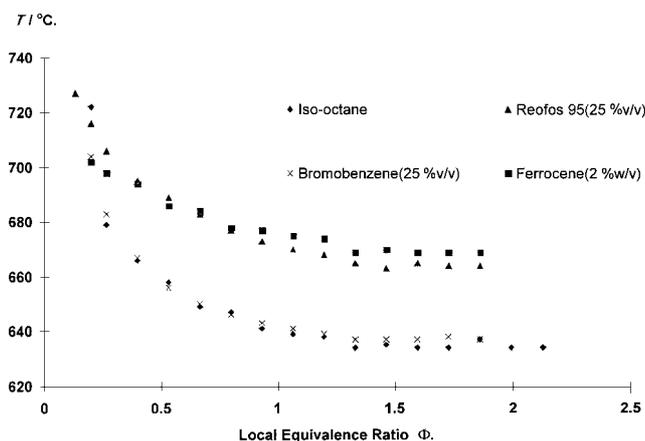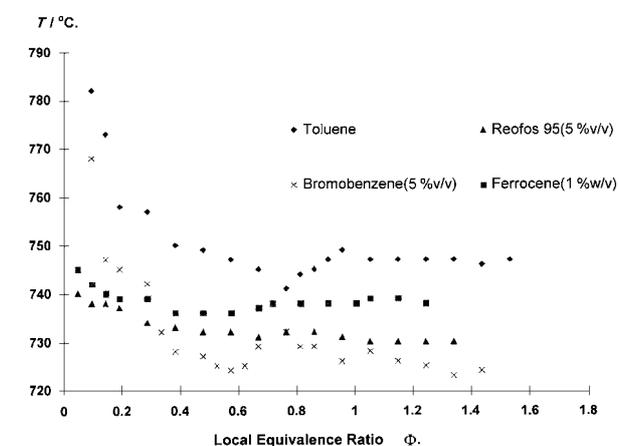
Figure 2. FTIR apparatus.

Figure 3. Ignition temperature versus LER for iso-octane (◆), iso-octane + ferrocene (1% w/v) (■), iso-octane + Reofos®95 (5% v/v) (▲) and iso-octane + bromobenzene (5% v/v) (×) in the vapour phase. Air flow $3 \, l\,min^{-1}$.
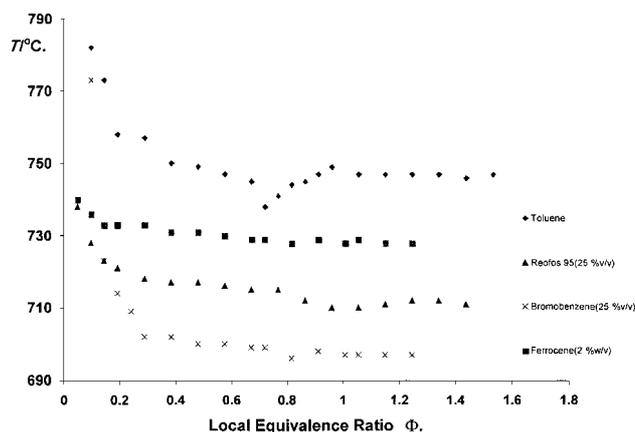
Figure 4. Ignition temperature versus, LER for iso-octane (◆), iso-octane + ferrocene (2% w/v) (■), iso-octane + Reofos® 95 (25% v/v) (▲) and iso-octane + bromobenzene (25% v/v) (×) in the vapour phase. Air flow 3lmin⁻¹.
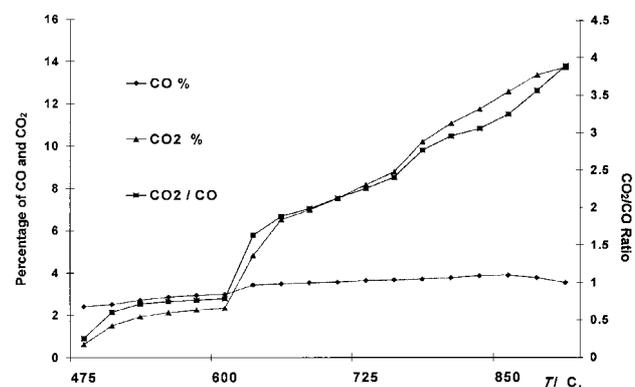

Figure 6. Ignition temperatures versus LER for toluene (◆), toluene + ferrocene (2% w/v) (■), toluene + Reofos 95 (25% v/v) (▲) and toluene + bromobenzene (25% v/v) (×) in the vapour phase. Airflow 3lmin⁻¹.

ture for iso-octane (ie ignitability was increased) whereas both ferrocene and Reofos® 95 raised the ignition temperature, corresponding to inhibition of ignition.

Figure 4 shows the results for the same additives at higher concentrations (25% (v/v) for Reofos® 95 and bromobenzene, and 2% (w/v) for ferrocene). Ferrocene and Reofos® 95 lead to even greater increases in ignition temperature of about 30°C; at these levels ferrocene had a slightly better overall performance than Reofos® 95, whereas bromobenzene showed little effect.

Addition of any of the fire-retardant additives to toluene as a fuel (Fig 5) lowered the ignition temperature across the entire stoichiometric range. Bromobenzene was slightly more effective at stoichiometries below 0.3 but was less effective over the rest of the stoichiometric range. Ferrocene and Reofos® 95 induced lower ignition temperatures than toluene alone, by a fairly constant amount across the stoichio-

metric range; these were about 16°C higher for ferrocene than for Reofos® 95.

With increased additive concentration (25% (v/v) for bromobenzene and Reofos® 95 and 2% (w/v) for ferrocene) for toluene (Fig 6), there was a further lowering of the ignition temperature. The patterns of response for both ferrocene and Reofos® 95 are similar to those in Fig 5; for Reofos® 95 ignition temperatures were lowered by a further 20°C to about 710°C near $\phi = 1$, whereas ferrocene caused a further 10°C fall to about 730°C near $\phi = 1$. Bromobenzene lowered the ignition temperature at this higher concentration to about 700°C across most of the stoichiometric range studied.

Gas analysis and FTIR studies of additive–iso-octane mixtures

Figure 7 shows the percentage of CO and CO_2 and the CO_2/CO ratio at $\phi = 1$ as a function of temperature. The CO percentage was fairly constant (around 3%) over the whole temperature range, and showed a small increase from 2% at 500°C to 3.5% at 900°C. The amount of CO_2, however, increased from 0.6% at 500°C to nearly fifteen times as much (7.3%) at 700°C and this figure was further doubled to 13.8% at

Figure 5. Ignition temperatures versus LER for toluene (◆), toluene + Ferrocene (1% w/v) (■), toluene + Reofos 95 (5% v/v) (▲) and toluene + Bromobenzene (5% v/v) (×) in the vapour phase. Air flow 3lmin⁻¹.

Figure 7. CO (◆) and CO_2 (▲) levels and CO_2/CO ratio (■) using TMP in air/N_2 mix; $\phi = 1$.
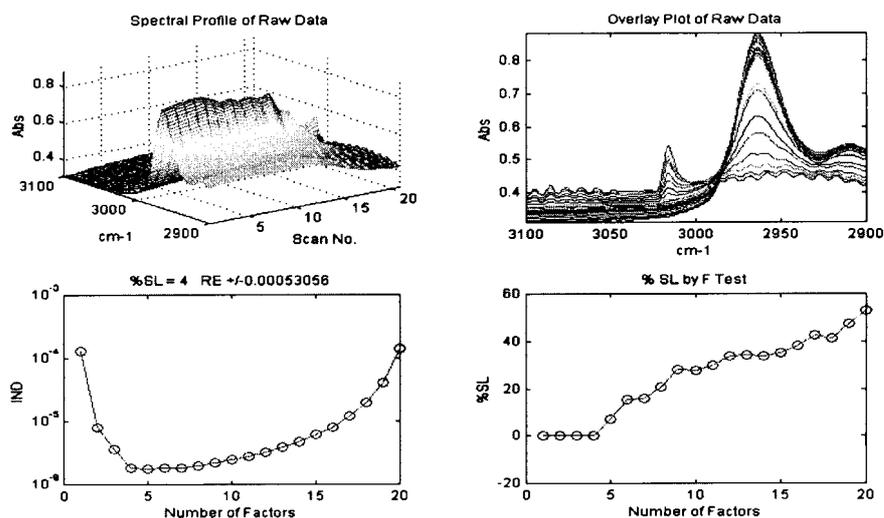
Figure 8. Typical data from chemometric software for iso-octane in air/N$_2$ mixture at 400–900 °C (ϕ = 1).

900 °C. The CO$_2$/CO ratio was always less than 4 across the entire temperature range, indicating that furnace conditions were typical of a smouldering or under-ventilated fire, ie the fire state most important in combustion toxicity because it mirrors known real-life fire conditions.

Figure 8 shows a typical chemometric analysis of part of the data, in this case for the 2900–3100 cm^{-1} region for iso-octane in an air/N$_2$ mix. The analysis was run on 21 FTIR spectral datasets at 25 °C intervals between 400 and 900 °C, using chemometric target factor analysis software described elsewhere.[18] The number of factors (four) is indicated by the minimum in the Malinowski indicator function (IND) and also by the increase above 5% in significance level for the *F*-test. This showed that four hydrocarbon components absorbing in the 2900–3100 cm^{-1} region were present.

The associated spectral profiles derived for these four factors or components for an iso-octane in air/N$_2$ mix are shown in Fig 9. The spectral profiles clearly show methane, alkane C—H stretching associated with iso-octane, and that two further molecules are present. On the basis of the known iso-octane oxidation chemistry, we assign these to vinyl C—H stretching absorption peaks,[30] most probably from 2-methylpropene and 2,4,4-trimethylpent-1-ene (or possibly propene) which are expected to be the major hydrocarbon products.[31] Because there is little absorption in the carbonyl stretching region of the spectra, it appears that formaldehyde or other aldehydes are not major products under these conditions.[31]

The relative concentration–temperature profiles for these four components over the range 400–900 °C are shown in Fig 10. The relative amount of iso-octane decreased slowly above 400 °C, and then sharply between 650 and 800 °C. The amount of methane formed was relatively small up to 650 °C and increased more rapidly thereafter. The two possible vinyl products were present in similar amounts. The amount of vinyl 1 steadily increased over the whole

temperature range, whereas vinyl 2 appeared to reach a maximum at about 825 °C. On this basis we can tentatively assign vinyl 1 to 2,4,4-trimethylpent-1-ene, because this is reported to reach a peak value at a lower temperature than 2-methyl propene,[31] which is assigned to vinyl 2. All data in Figs 8–10 were obtained with ϕ = 1.
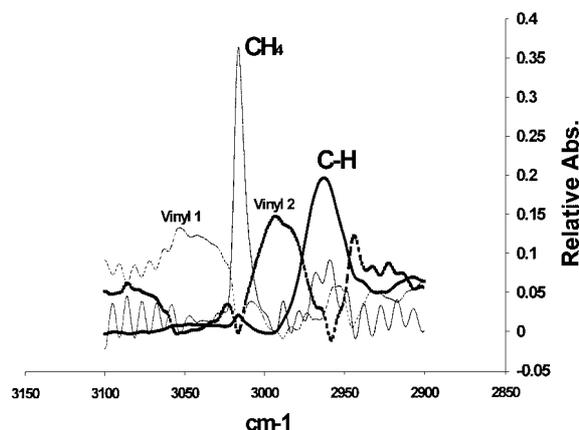

Figure 9. Spectral profile of iso-octane in the 2850–3150 cm^{-1} range, ϕ = 1, no additive.
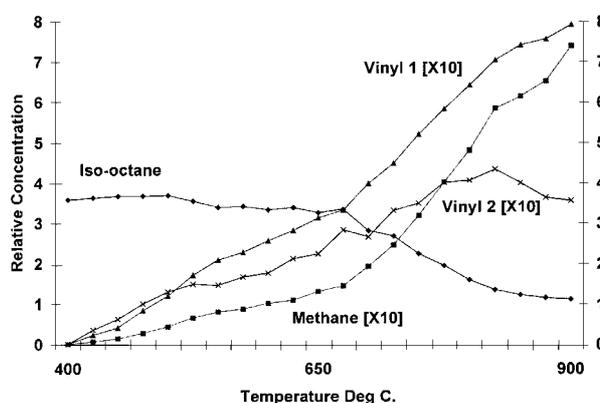

Figure 10. Reactant (iso-octane, ◆) and product profile (vinyl 1, ▲; vinyl 2, ×; methane, ■) (ϕ = 1).

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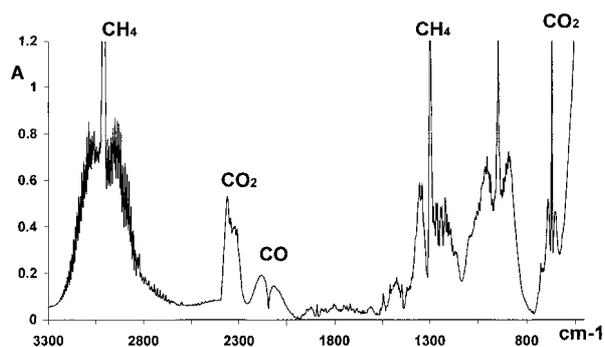
Figure 11. Typical FTIR spectrum for products from TMP in air/N$_2$ mix at 750°C ($\phi = 1$).

Figure 12. Spectral profile in the 1100–1200 cm^{-1} region of an Iso-octane/TMP (5% v/v) mixture in air/N$_2$ ($\phi = 1$).

A typical FTIR spectrum for the products from TMP only (in an air/N$_2$ mix at 750°C, $\phi = 1$) is shown in Fig 11. Large peaks are seen at round 2800–3200 cm^{-1}, indicating methane, with P, Q and R branches clearly shown; at about 1300 cm^{-1} P, Q and R branches of the molecule methane are also seen; the same branching is shown around 700 cm^{-1} for CO$_2$. It is clear that these major features covering fairly wide regions of the spectrum, prevent traditional analysis from identifying any other bands which they obscure. This has led to the use of the chemometric software[18] which allows other species below (or covered by) the major spectral features in the same region to be identified. The assignments of the major peaks in these spectra (aided by use of the chemometric software), of which Fig 11 is an example only, are given in Table 1.

To investigate whether the intermediate phosphorus-containing species which may play a role in flame chemistry and retardancy, could be detected, spectral profiles for the region 1100–1200 c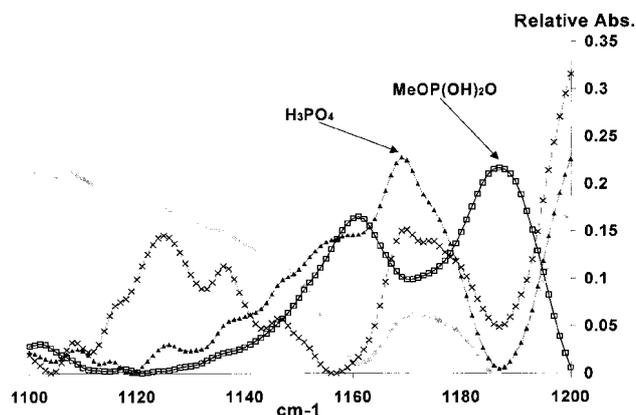m^{-1}, corresponding to the P—O absorption region were analysed for TMP data. Factor analysis indicates that four components are present, and the spectral profiles of these components in this region are shown in Fig 12. One product with an absorption peak at 1187 cm^{-1} is assigned to MeOP(OH)$_2$O,[32] and a second peak at 1170 cm^{-1} is assigned to H$_3$PO$_4$.[32] (MeO)$_2$P(OH)O was assigned to a peak of 1211 cm^{-1} (not shown), indicating that the progressive oxidation of TMP to *ortho*-phosphoric acid can be monitored. Calculations of gas-phase geometries and vibrational frequencies were carried out using Hartree–Fock theory with a 3-21G basis set, using the Gaussian 98 quantum mechanical package. The frequencies were scaled using a typical factor of 0.89 and the wavenumbers predicted[32] are shown in Table 2.

The values compare reasonably well (given the low level of the calculation) with the derived peak wavenumbers of 1170, 1187 and 1211 cm^{-1}, respectively. A more sophisticated analysis is being undertaken.

Table 1. Summary of peak assignments from analysis of chemometric data

Peak (cm^{-1})	Assignment	Comments
515	POHO	Ref 35,
667	CO$_2$	
950	P—O	Ref 35,
988, 998	POHO	
1170	H$_3$PO$_4$	Ref 32,
1187	CH$_3$OP(OH)$_2$O	Ref 32,
1211	(CH$_3$O)$_2$P(OH)O	Ref 32,
1221, 1270	P=O	Stretch
1304	CH$_4$	
1355	CH$_3$	Symmetrical deformation
1733	POHO	Ref 35,
2143	CO	
2344	POHO	Ref 35,
2349	CO$_2$	
2558	POH	Ref 35,
2948, 2958	C—H	Symmetrical and asymmetrical stretch
2989	CH$_3$ and CH$_2$	Aliphatic
3016	CH$_4$	
3058	CH$_2$	Vinyl CH stretch

Table 2. Predicted wavenumbers for intermediate phosphorus-containing species

| Product	Predicted wavenumber (cm^{-1})
H_3PO_4	1176
$MeOP(OH)_2O$	1185
$(MeO)_2P(OH)O$	1187

DISCUSSION

The results show that both ferrocene and Reofos[®] 95 raise the ignition temperature of iso-octane and that this effect increases with increased concentration, whereas bromobenzene has little effect or a negative effect. For toluene, all the additives studied lowered the ignition temperature, ie increased the flammability of the toluene. This appears to suggest that ferrocene and Reofos[®] 95 may be effective flame retardants in the gas phase for aliphatic fuels, but may be less effective for aromatic fuels. It may be that ferrocene, or a degradation product of ferrocene, acts as a radical trap to produce stable radicals during the early stages of iso-octane decomposition:

$$FcH + R\cdot \rightarrow FcH—R\cdot \qquad (1)$$
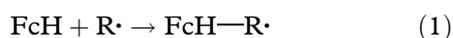
effectively slowing down the degradation of iso-octane, resulting in higher ignition temperatures. Similarly Reofos[®] 95 could act as a radical trap:

$$(RO)_3P{=}O + R\cdot \rightarrow (RO)_3P—OR\cdot \qquad (2)$$
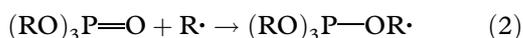
In the case of toluene, however, it is possible that degradation is initiated by ferrocene or Reofos[®] 95, through a bimolecular reaction:
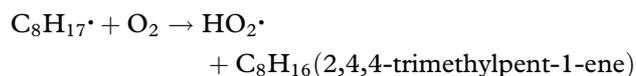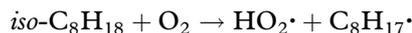
$$FcH + RH \rightarrow FcH—H\cdot + R\cdot \qquad (3)$$

$$(RO)_3P{=}O + RH \rightarrow (RO)_3P—OH\cdot + R\cdot \qquad (4)$$
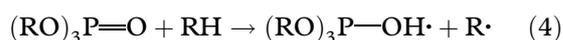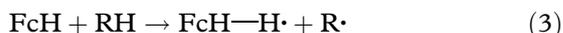
In the early stages of reaction, R·would represent a number of possible radicals including $C_4H_9\cdot$, $C_8H_{17}\cdot$ from iso-octane, and $C_6H_5CH_2\cdot$ from toluene: it is possible that this is due to the ease with which toluene can form the relatively stable benzyl radical (stabilization energy $80\,kJ\,mol^{-1}$).[33]

The FTIR study shows that after combustion there are several hydrocarbons (C—H) and phosphorus (P—O) species, together with carbon monoxide and carbon dioxide. Four major hydrocarbon compounds are present including iso-octane, methane and two vinyl compounds. One of these may be anticipated to be 2-methylpropene, because this would be expected to form from the relatively stable *tert*-butyl radical which would be expected to be formed during oxidative pyrolysis.
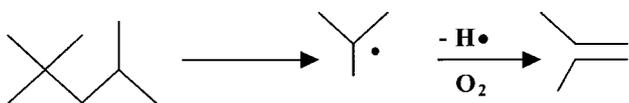

The other alkene could be either 2,4,4-trimethyl-

pent-1-ene, formed through reactions

$$iso\text{-}C_8H_{18} + O_2 \rightarrow HO_2\cdot + C_8H_{17}\cdot$$

$$C_8H_{17}\cdot + O_2 \rightarrow HO_2\cdot$$
$$+ C_8H_{16}(2,4,4\text{-trimethylpent-1-ene})$$

or propene which is also formed in substantial amounts.[31] These alkene products are expected to increase to a maximum concentration before undergoing oxidative pyrolysis at higher temperatures. This is generally reflected in the increasing concentrations of CO_2 at higher temperatures through increasing oxidation of the hydrocarbon species present. At lower temperatures, lower CO_2/CO ratios are consistent with a limited extent of oxidation. The concentration of methane steadily increases over the whole temperature range, reflecting the relative stability of smaller hydrocarbon product molecules. The results also indicate that for TMP, four major P—O containing compounds are present, possibly including two intermediate products. The structure of TMP (**II**) is shown.

(**II**)   (**III**)
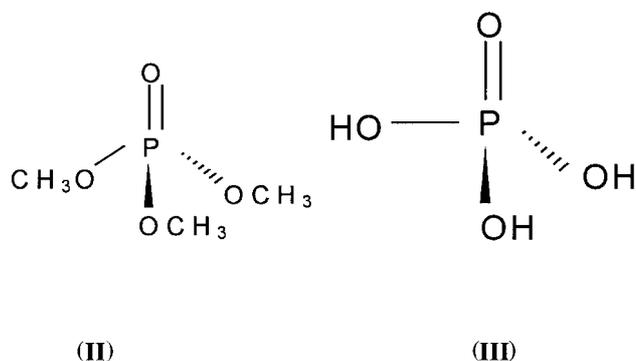
Green[3] implied that phosphoric acid is implicated in the gas-phase action of a fire retardant containing phosphorus. Both TMP and the Reofos[®] compounds would be expected to form *ortho*-phosphoric acid (**III**) as the final combustion product in well oxygenated conditions, via several partially oxidized intermediates (**IV** and **V**). This posssible mechanism route has also been suggested by Korobeinichev *et al*[34]

(**IV**)   (**V**)
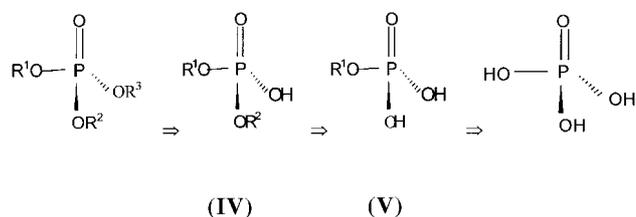
Evidence for the intermediates **IV** and **V** is obtained from their peak absorbances in Fig 12, and assignments are based on the calculations of Withnall.[32]

CONCLUSIONS AND FURTHER WORK

Ignition temperature studies suggest that Reofos[®] 95 and ferrocene, but not bromobenzene, are effective as

gas-phase fire-retardant additives with iso-octane. All the additives studied showed a negative effect with toluene, lowering the ignition temperature.

FTIR combined with chemometric software has been demonstrated to be a potentially very important tool for the analysis of fire-retardant mechanisms in the gas phase, and it may well be possible to improve our understanding of the mechanistic processes occurring for a variety of fire-retardant additives.

Further work is in progress on the identification of the intermediates species formed during TMP degradation. It is also planned to use a wider range of both fuels and additives to obtain a more detailed data set for kinetic analysis and to assess more fully the applicability of the chemometric method.

ACKNOWLEDGEMENTS

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