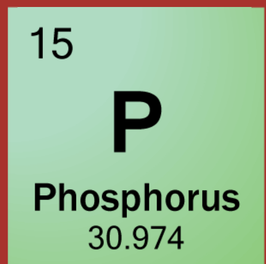
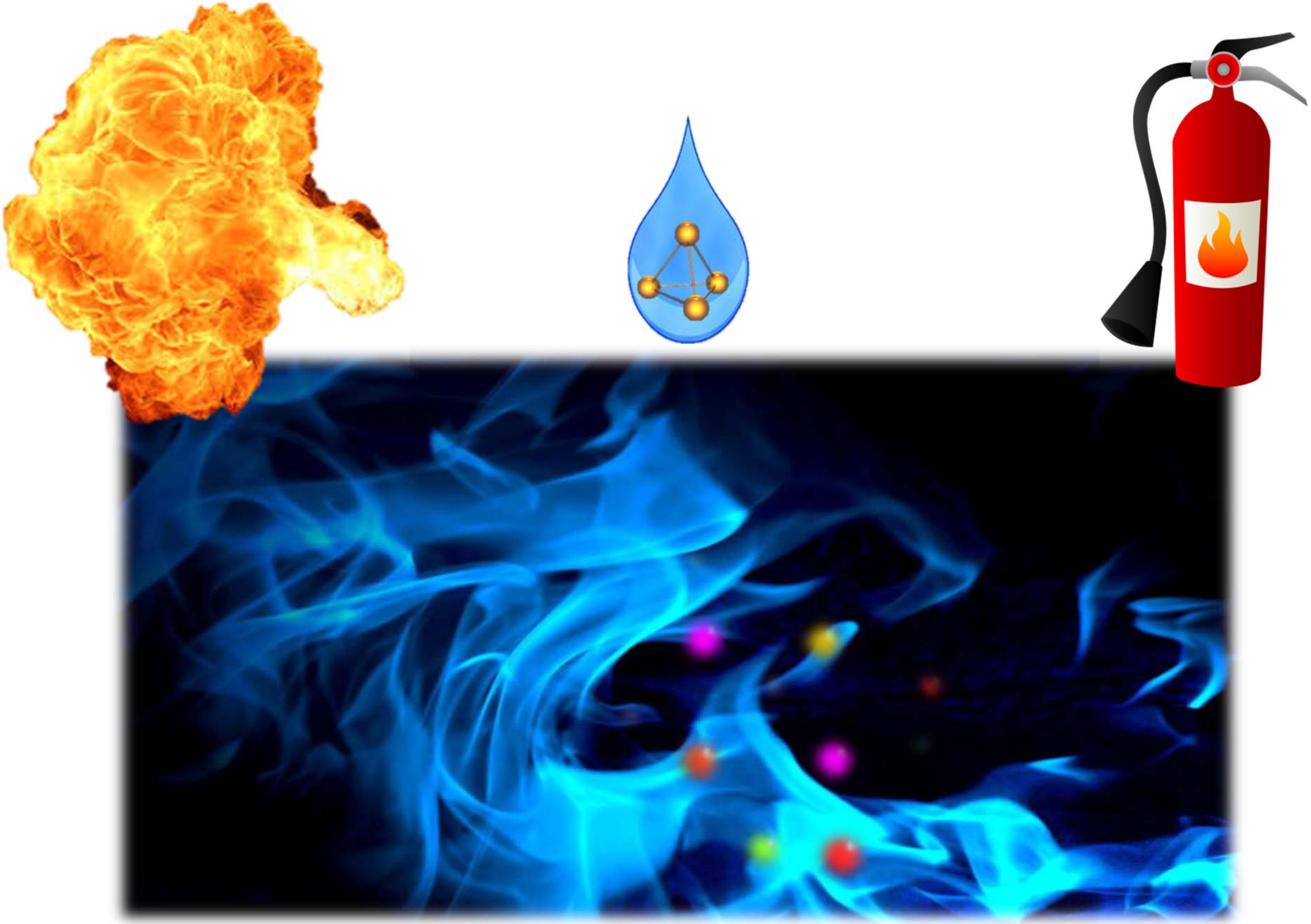
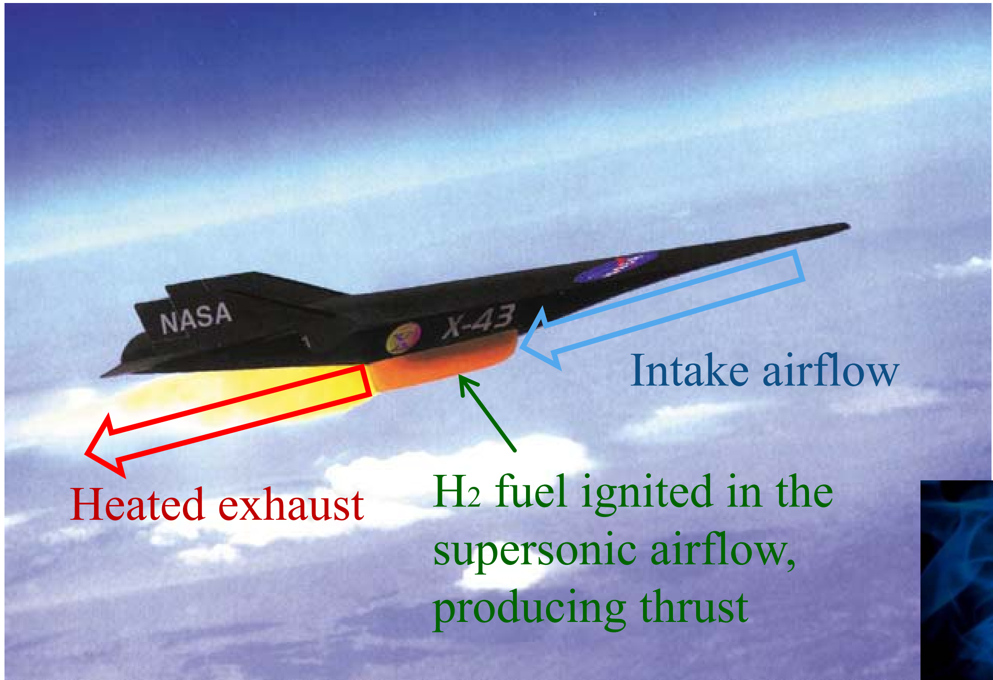
ETH Zürich, Laboratory of inorganic chemistry
Empa, Laboratory of advanced fibers



14.03.2017
Shuyu Liang

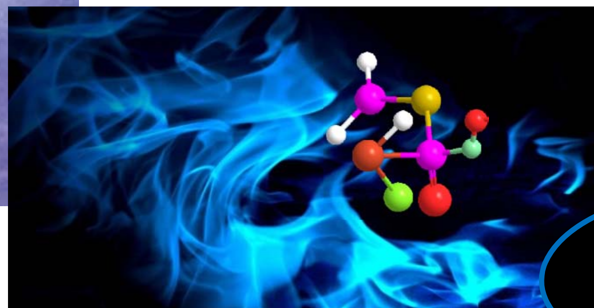


Gas-Phase-Active Phosphorus Intermediates



NASA: Scramjet Engine

Energy gain from accident prevention

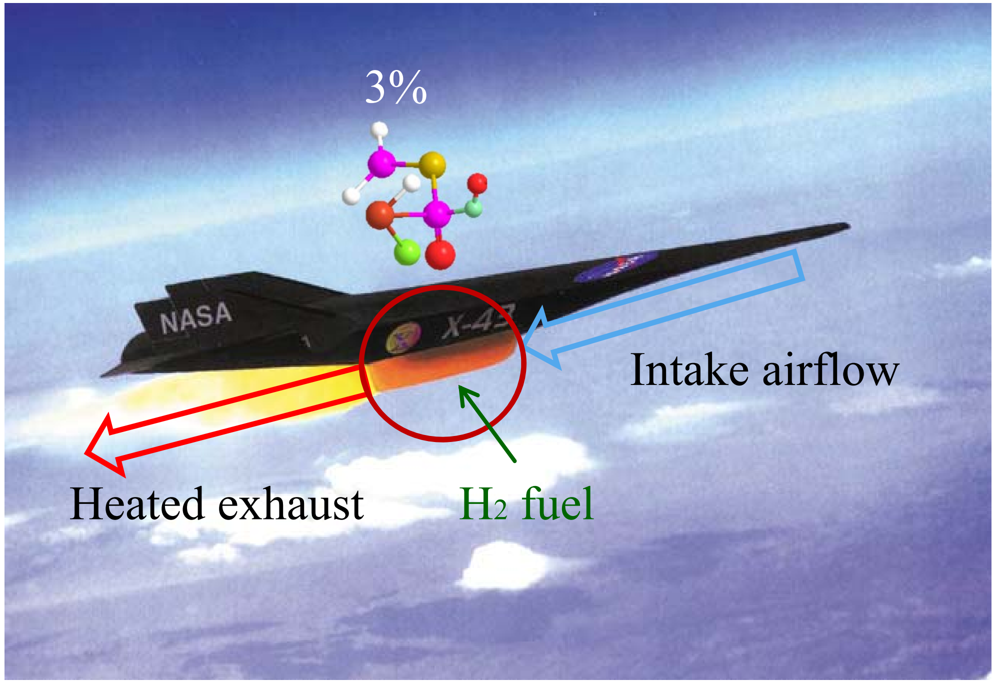


P waste Incineration

Phosphorus additive

1. Background: Chemistry
2. State-of-art
3. Imaging Photoelectron Photoion Coincidence (iPEPICO)
4. Results and discussions
5. Outlook

Combustion Kick



$2H_2 + O_2 \rightarrow 2H_2O$

Initiation $H_2 \rightarrow 2{*}H$; $O_2 \rightarrow 2{*}O$

Chain branching $O_2 + H \rightarrow {*}OH + {*}O$

$H_2 + {*}O \rightarrow {*}OH + {*}H$

Chain Propagation: $H_2 + {*}OH \rightarrow H_2O + {*}H$

Chain termination: ${*}H + \text{wall} \rightarrow H_2$

${*}H + O_2 + M \rightarrow HO_2 + M$, etc.

${*}H + {*}OH \rightarrow H_2O$ [1]

Aircraft or rocket propulsion systems : Hydrogen fuel

Catalytic effect of phosphorus species enhances the fuel efficiency → O_2 ${*}H$ $HOPO$ ${*}PO_2$ H_2 ${*}OH$ ${*}O$ $HOPO_2$ ${*}HO_2$ HPO →

$H + PO_2 \rightarrow HOPO$

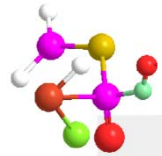
$H + HOPO \rightarrow H_2 + PO_2$

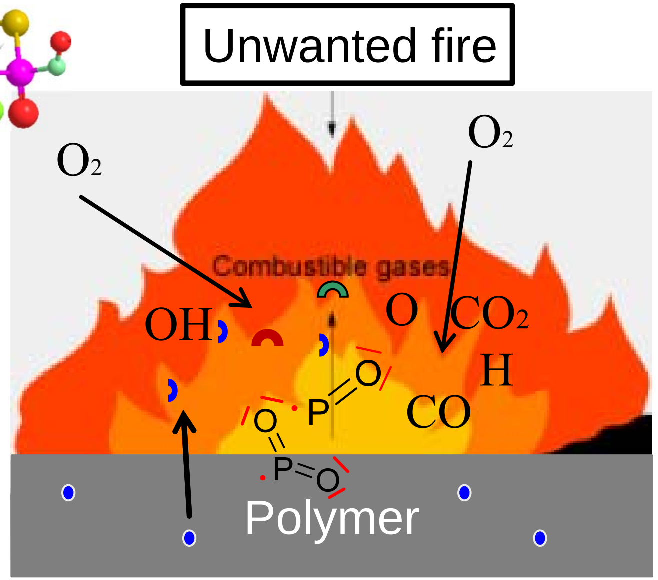
$OH + H_2 \rightarrow H_2O + H$

etc. [2]

[1] Combustion Chemistry, Chapter 3, AER 1304 – ÖLG
[2] A. Twarowski, Combustion and Flame 1995, 102, 41-54.

Flame inhibition





Polymer decomposed into fuels ($C_xH_y(O_z)$) [1]

Initiation:

1. $C_xH_y + M \rightarrow$ daugther radicals $+ M \rightarrow$ olefins $+ H + M$
2. $H^* + O_2 \rightarrow {}^*O + {}^*OH$

Propagation:

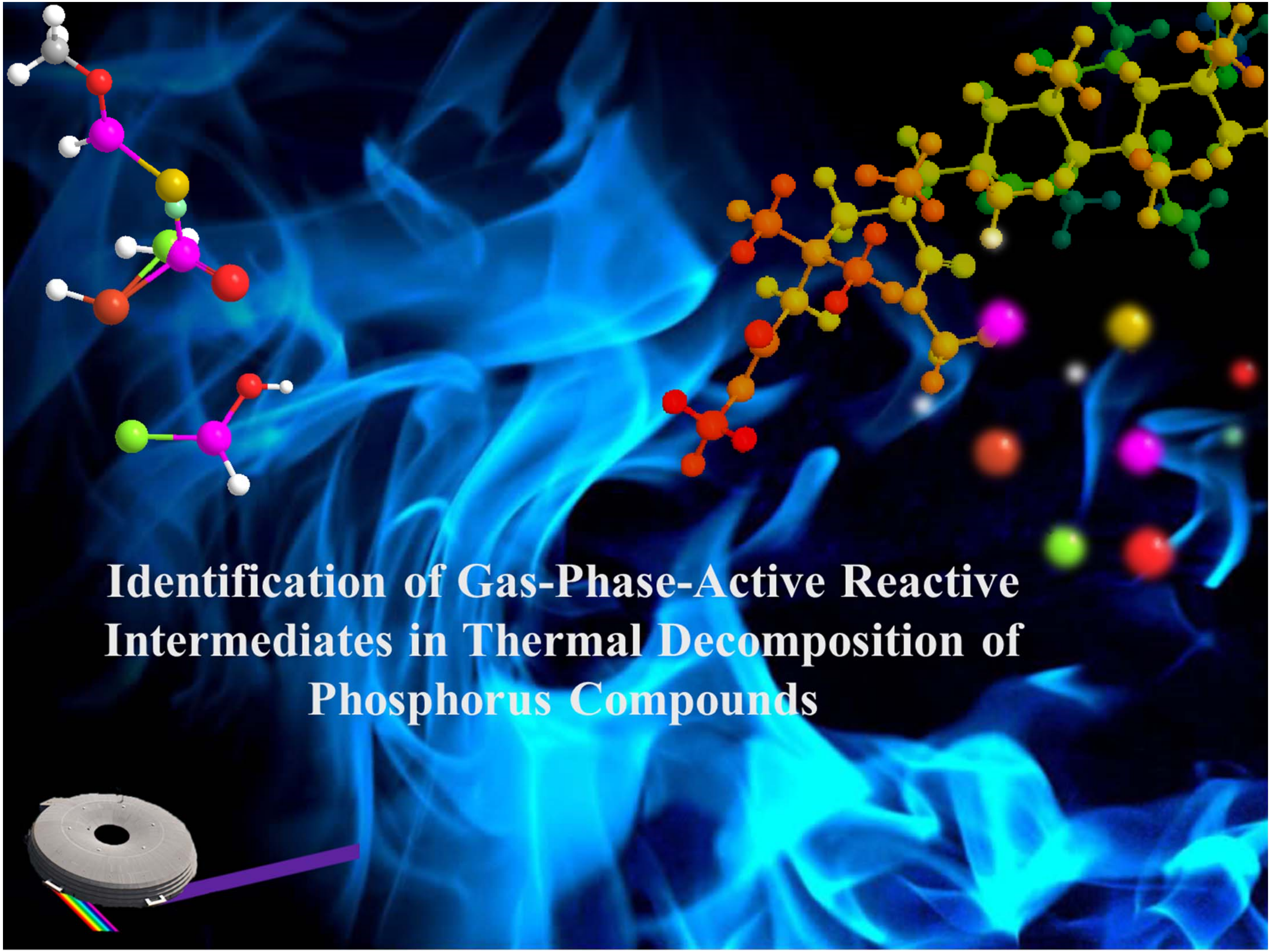
3. $C_xH_y + {}^*H \rightarrow C_xH_{y-1} + H_2$
   $C_xH_y + {}^*O \rightarrow C_xH_{y-1} + {}^*OH$
   $C_xH_y + {}^*OH \rightarrow C_xH_{y-1} + H_2O$
4. $C_xH_{y-1} + M \rightarrow$ olefin $+ {}^*H$
   olefin(s) $+ {}^*O \rightarrow \rightarrow \rightarrow CO + {}^*H + C_mH_n$
5. ${}^*O + H_2O \rightarrow 2{}^*OH$
   $CO + {}^*OH \rightarrow CO_2 + {}^*H$ (key step for heat release)
   ${}^*H + O_2 \rightarrow {}^*O + {}^*OH$

Termination:

6. ${}^*H + \text{Wall} \rightarrow H_2$
   ${}^*H + O_2 \rightarrow {}^*O_2H$

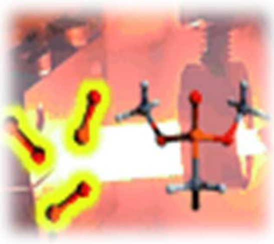
${}^*H + PO_2 \rightarrow HOPO$
${}^*H + HOPO \rightarrow H_2 + PO_2$
${}^*OH + HOPO \rightarrow H_2O + PO_2$
${}^*O + HOPO \rightarrow PO_2 + {}^*OH$
etc. [1,3]

[1] Combustion Chemistry, Chapter 3, AER 1304 – ÖLG
[3] F. Takahashi, V. Katta, G. Linteris and V. Babushok. *Fire Science and Technology*, 751-758 (2015).


Identification of Gas-Phase-Active Reactive Intermediates in Thermal Decomposition of Phosphorus Compounds

State of the art instrumentations

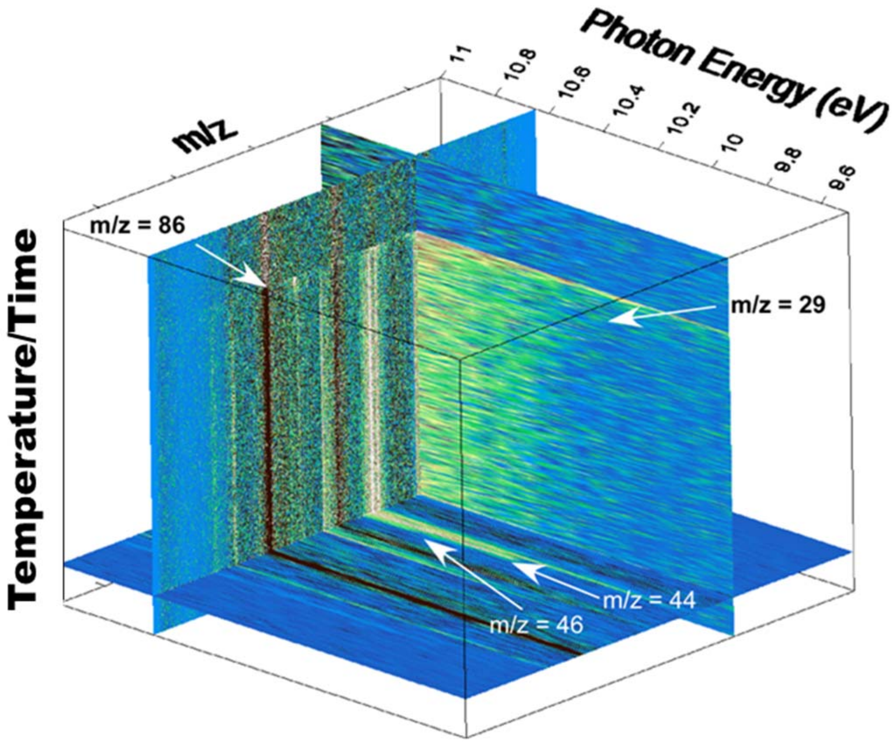
1. Chemical synthesis – Heating tube coupled with chromatography (GC) and titration.
2. Flame retardant mechanism – Pyrolysis – Electron ionization (EI) based GC-mass spectrometry (MS)
3. Incineration of warfare agent – Combustion – Fourier-transform infrared spectroscopy
4. Enhancement of fuel efficiency – Combustion – Eximer laser based absorption spectroscopy– hydrogen fuel studies (*H, *OH) in presence of phosphine
5. Destruction chemistry of OPC – Burner – Molecular beam mass spectrometry (MBMS)
6. Inhibition effect of combustible radicals – Burner – Laser induced fluorescence spectroscopy (LIF) (mainly on *H, *OH)



[4] K. Salmeia, J. Fage, S. Liang and S. Gaan, Polymers 2015, 7, 504.

Photoionization mass (spectrometry) + spectroscopy

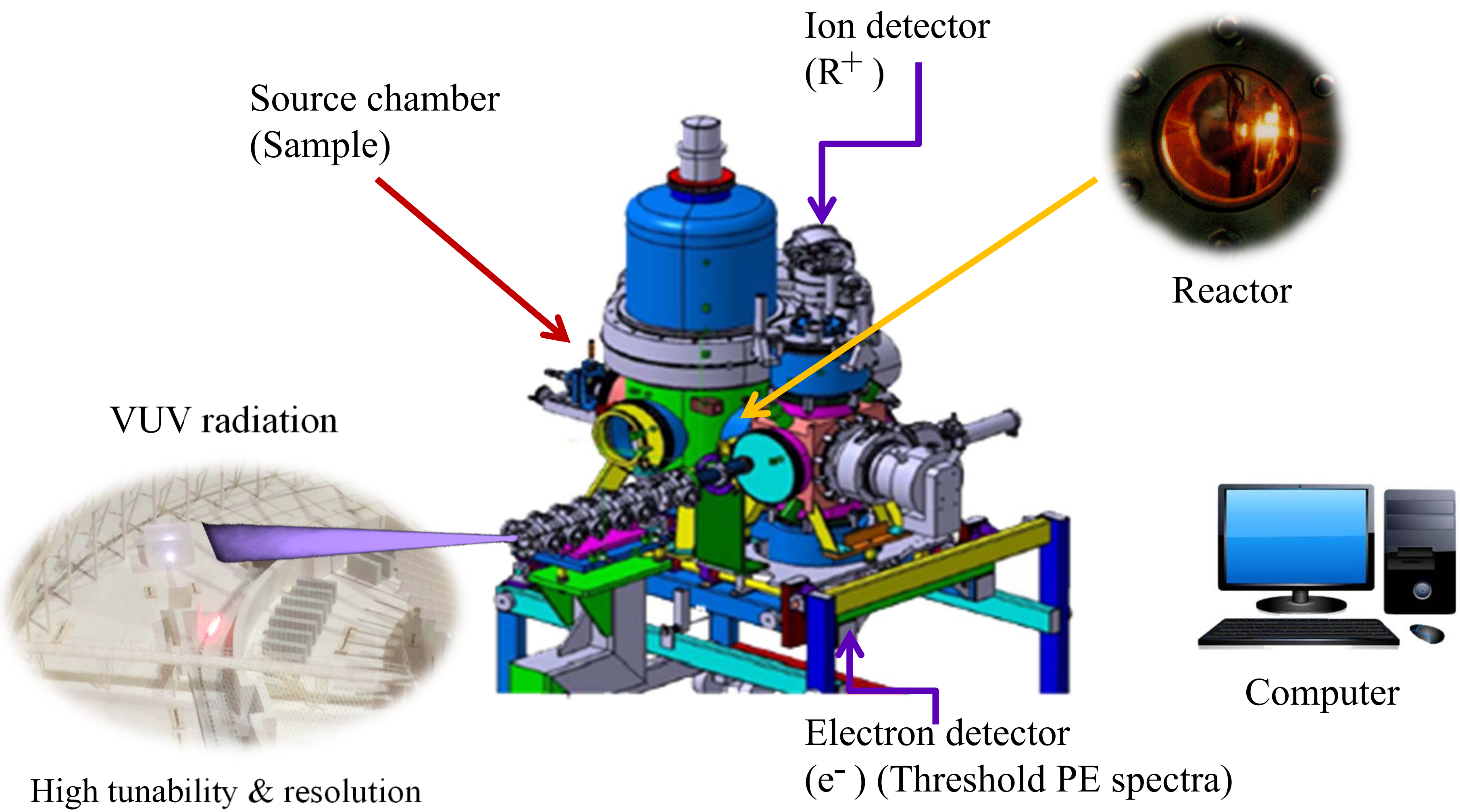
1.Multiplexed mass spectrometry (simultaneously detecting many masses)
2.Photoionization by tunable synchrotron radiation, which provides isomeric specifity through the photoionization spectroscopy



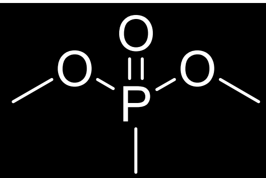
The data can be correlated and integrated alone different dimensions

Experimental Setup:

Image photoelectron photoion coincidence (iPEPICO) Endstation +
Vacuum ultraviolet radiation +
Reactor

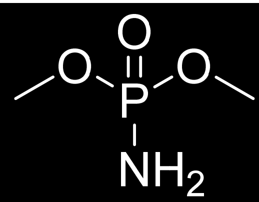


Model compounds



Dimethyl methyl phosphonate (DMMP)

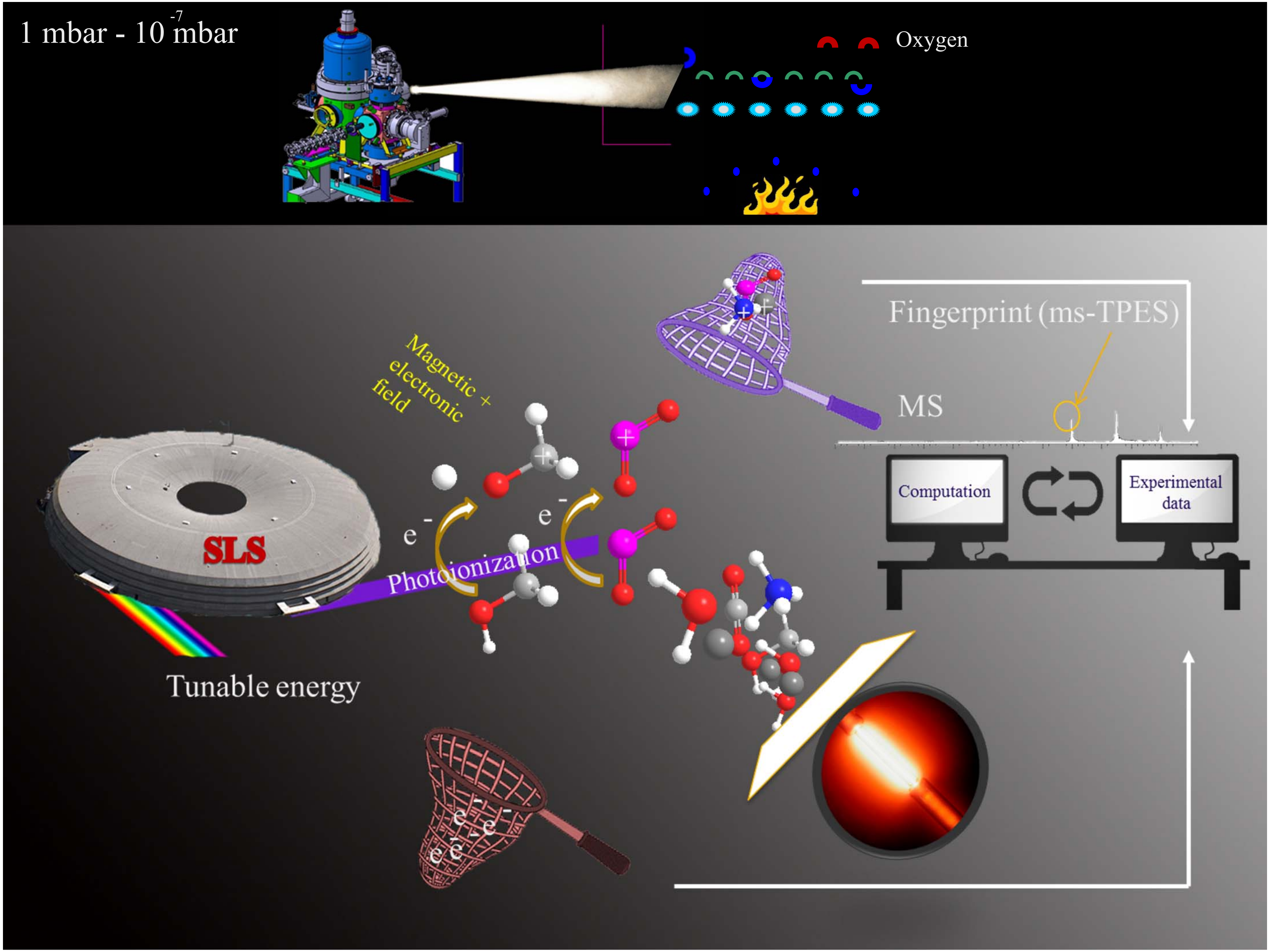
- Structural simplicity
- Limited toxicity issue
- Proper vapor pressure
- Model compound in previous inhibition and combustion studies: (known precursor to the inhibitor *PO, $*PO_2$)



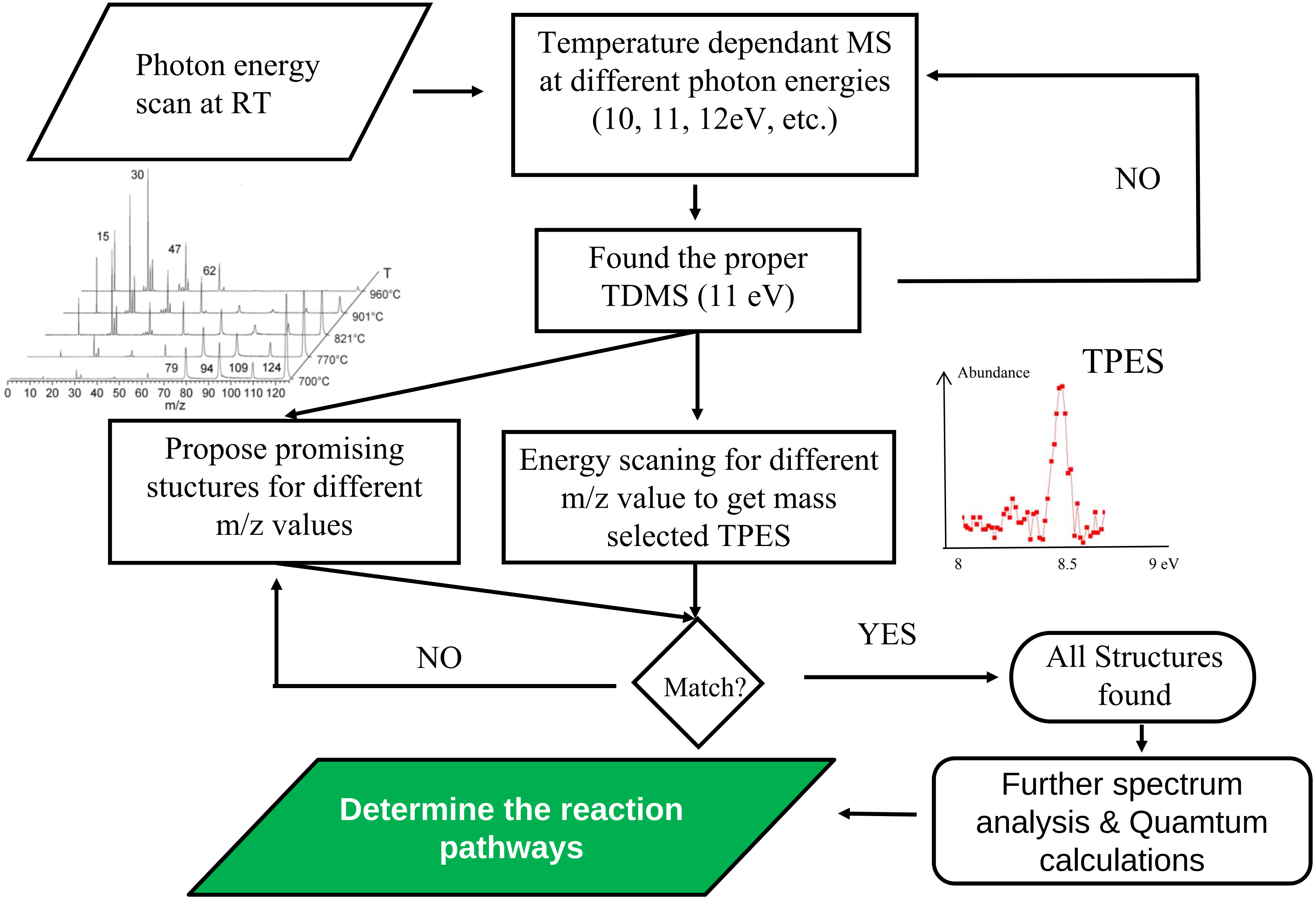
Dimethyl phosphoramidate (DMPR)

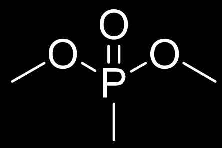
- OPC category of lower toxicity
- Structural similarity to DMMP
- Potential PN synergistic effect in flame inhibition/promotion

DMMP/DMPR was seeded in Argon carrying gas in a heated sample container (0.1-1%) and expanded through a 100-µm nozzle into the pyrolysis reactor, where the temperature can be monitored.



1 mbar - 10^{-7} mbar
Oxygen
Magnetic + electronic field
Fingerprint (ms-TPES)
MS
Computation
Experimental data
SLS
Photoionization
Tunable energy


Photon energy scan at RT
Temperature dependant MS at different photon energies (10, 11, 12eV, etc.)
NO
Found the proper TDMS (11 eV)
30
15
47
62
T
960°C
901°C
821°C
770°C
700°C
79
94
109
124
0 10 20 30 40 50 60 70 80 90 100 110 120
m/z
TPES
Abundance
8
8.5
9 eV
Propose promising stuctures for different m/z values
Energy scaning for different m/z value to get mass selected TPES
NO
Match?
YES
All Structures found
Further spectrum analysis & Quamtum calculations
Determine the reaction pathways



Dimethyl methyl phosphonate (DMMP) m/z = 124
0.33% in Argon molecular beam

Photoionization experiment at room temperature - control experiments.

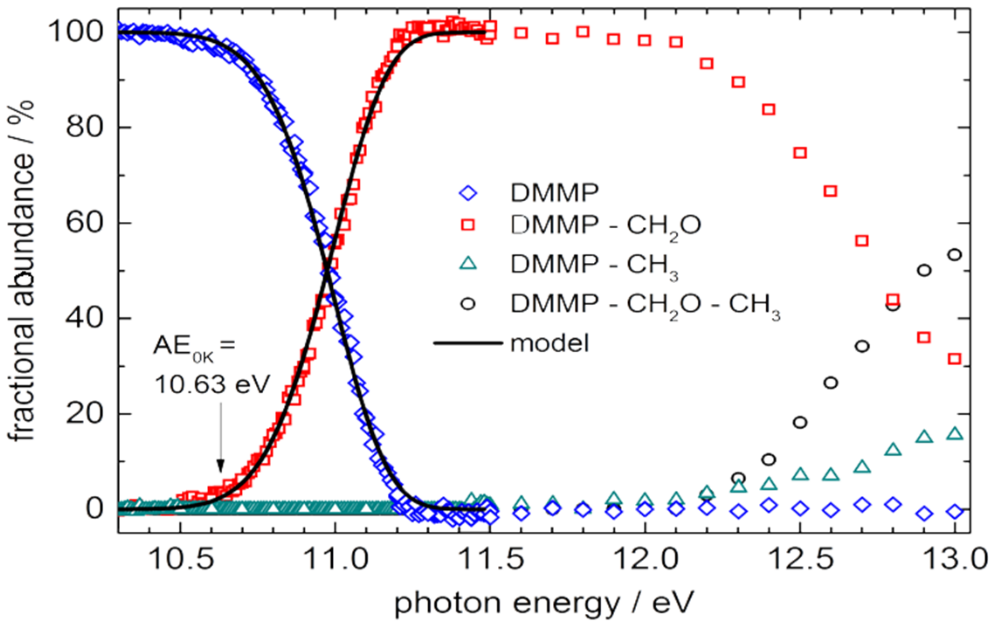
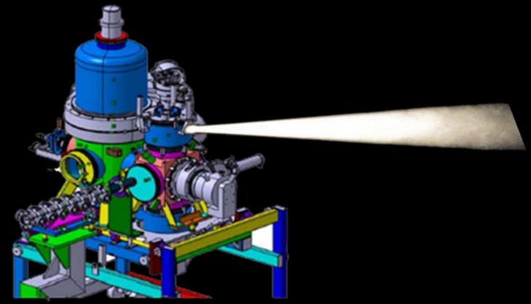


Fig. 1: Breakdown diagram of DMMP at room temperature (dissociative ionization).

TD-tof-MS



m/z 30

m/z 15

m/z 47 ?

m/z 47

m/z 62 ?

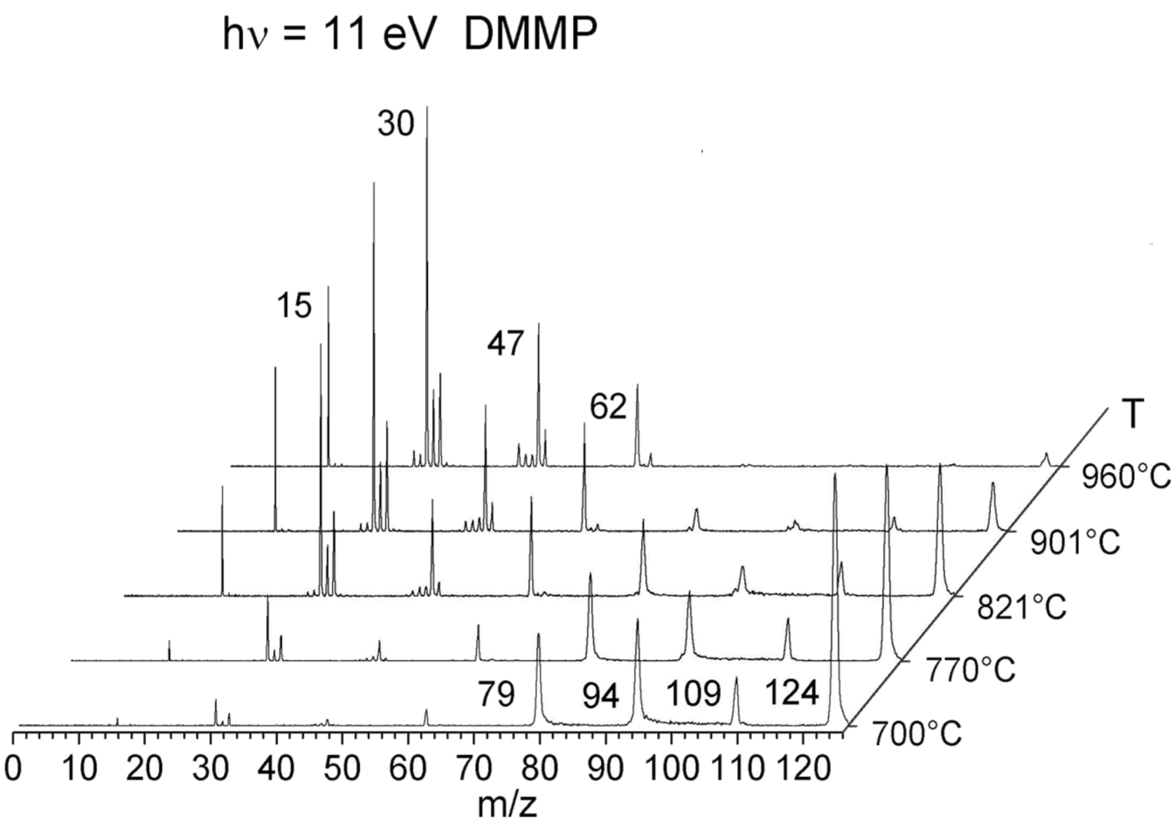
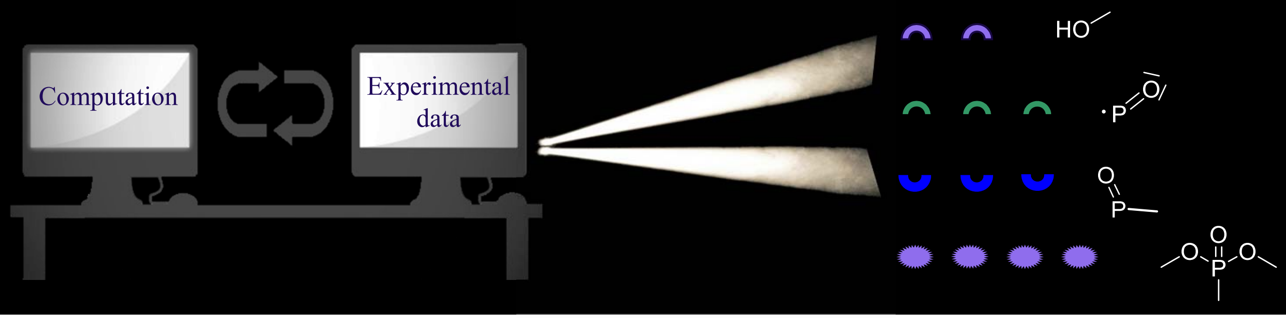


Fig. 2 Temperature dependent time-of-flight mass spectrum of DMMP at 11eV.

ms-TPES



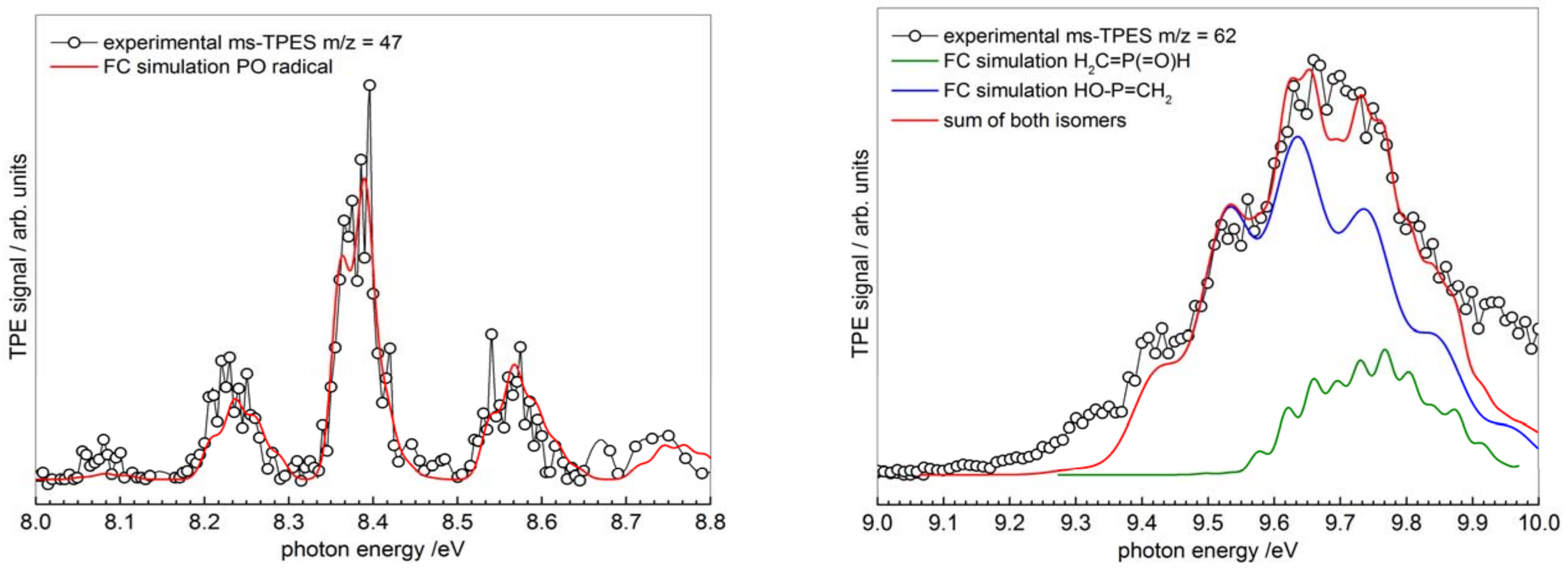
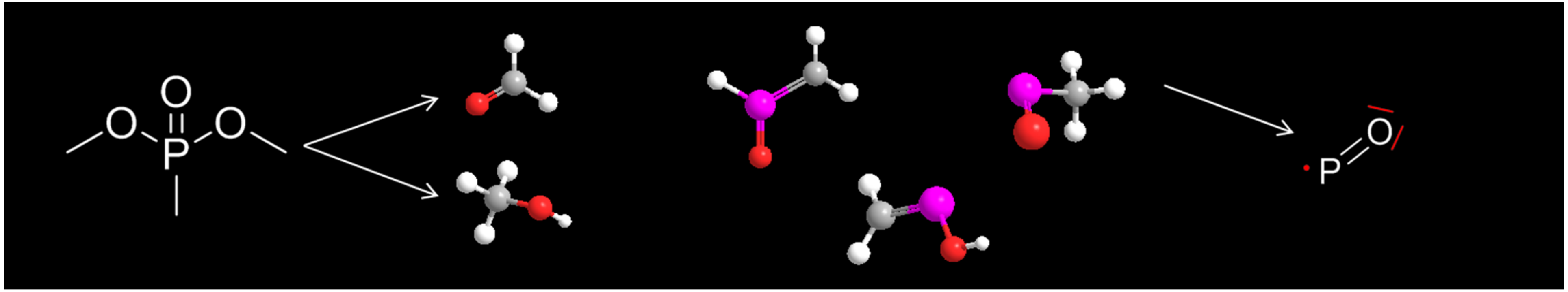
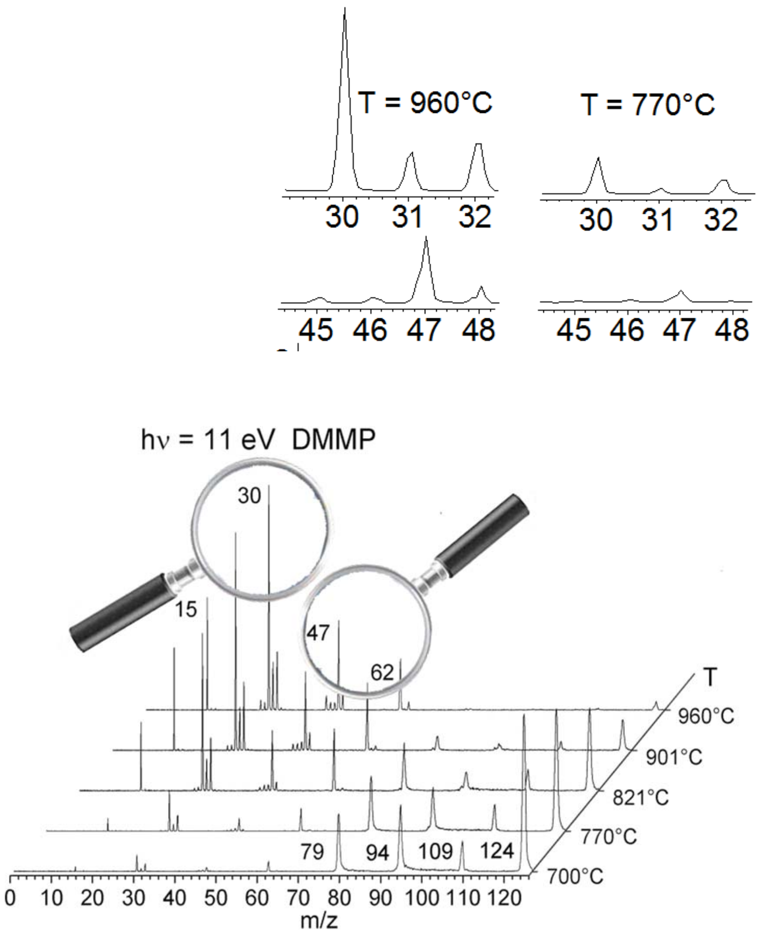


Fig. 3 Mass selected- threshold photoelectron spectra of m/z 47 and m/z 62 at 900°C (experimental and simulated spectra)





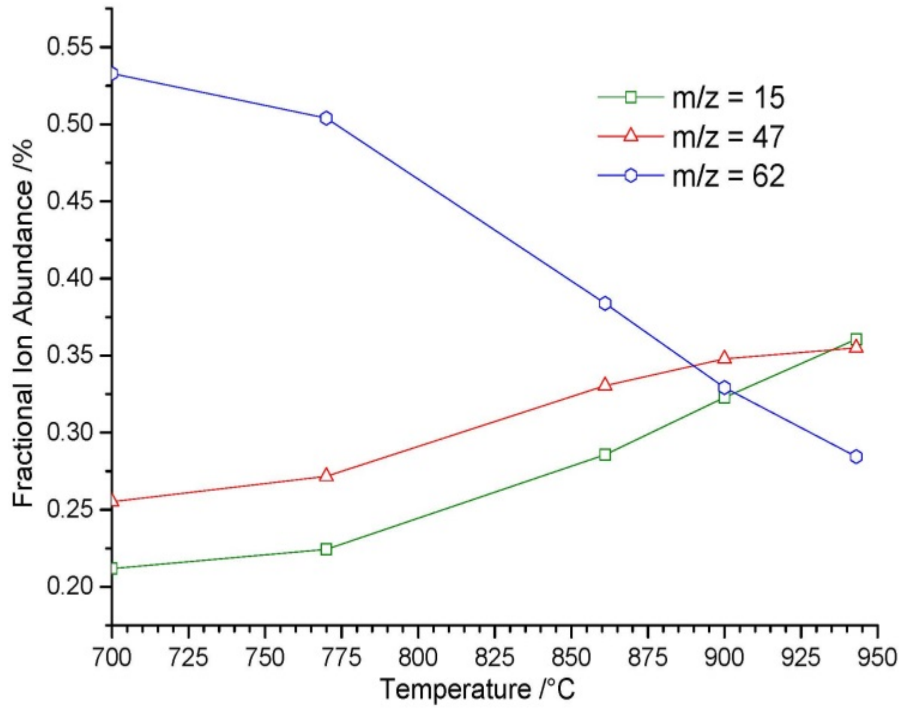
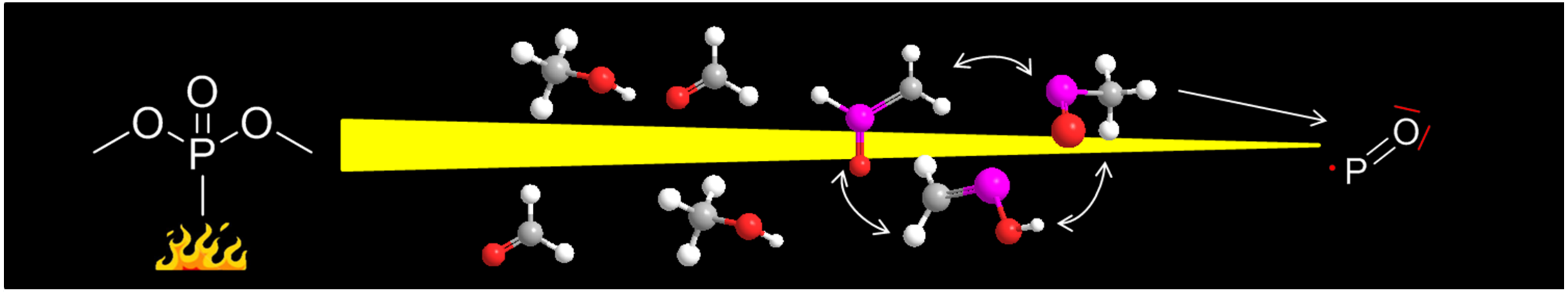
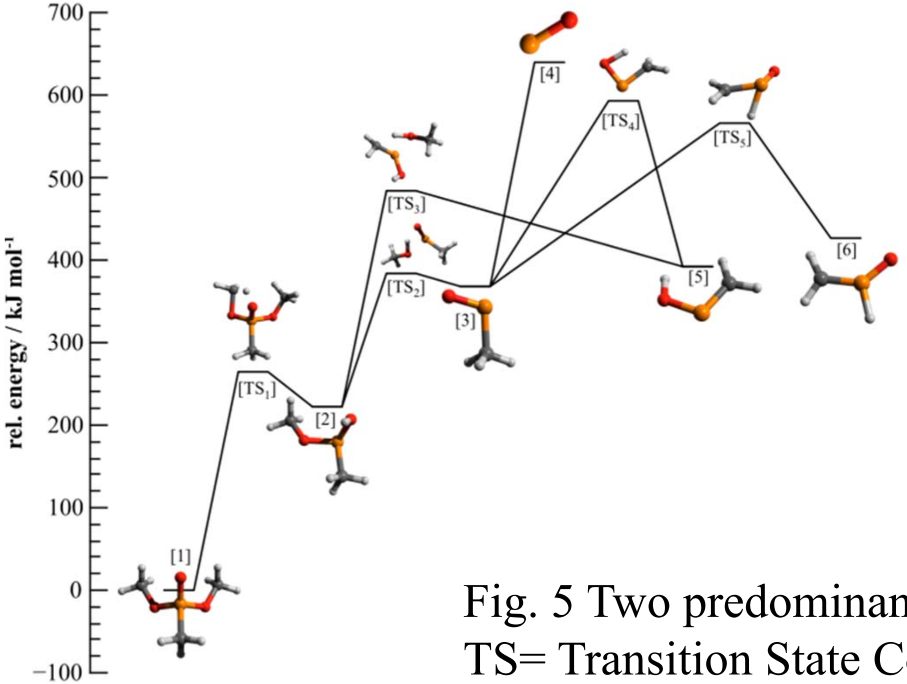


Fig. 4 Breakdown diagram of m/z = 62 (Pyrolysis)



Together with a comprehensive CBS-QB3 treatise of the potential energy surface, we propose two predominant decomposition pathways



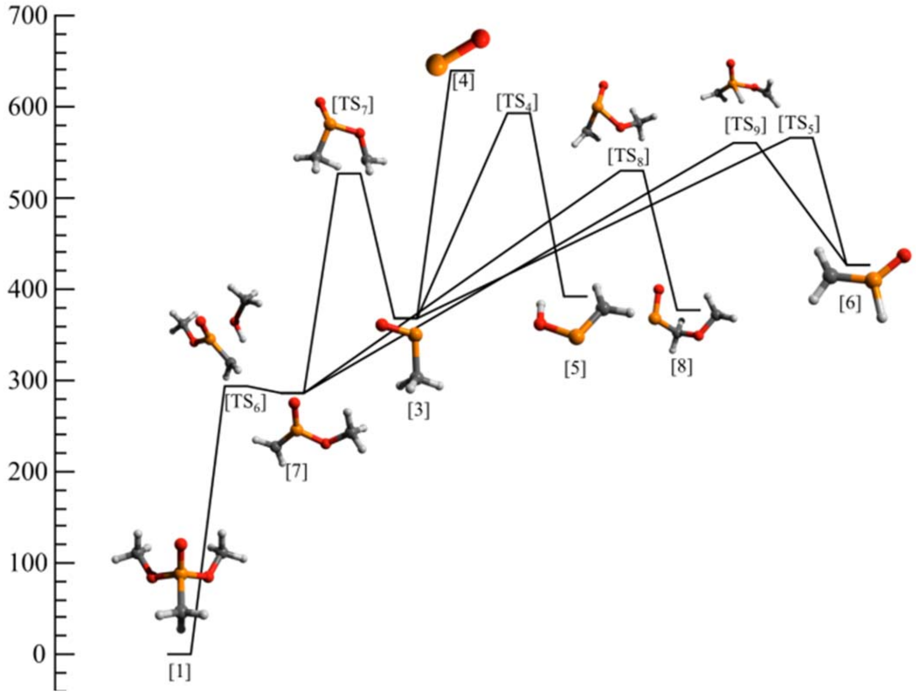
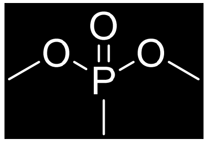
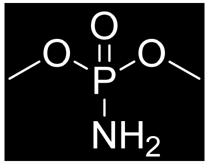


Fig. 5 Two predominant pathways of thermal decomposition of DMMP
TS= Transition State Complex

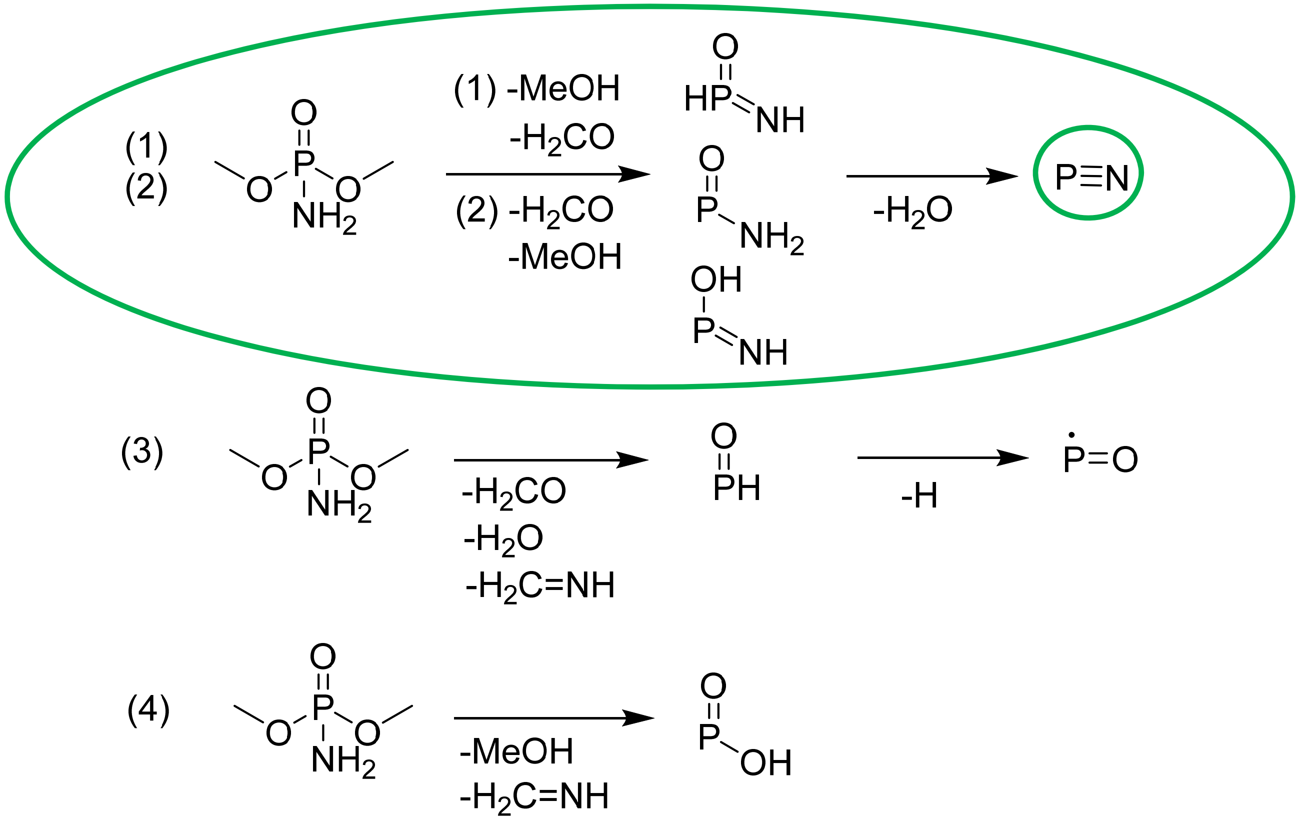


- Thermal decomposition of DMMP starts at around 700° C. The PO radicals and their immediate precursors are observed, while PO_2 is not detected.
- Three elusive CH_3OP isomers have been identified as tautomers $H_2C{=}P{-}OH$, $H_2C{=}P({=}O)H$ and $O{=}P{-}CH_3$ which leads to the final PO radical formation.
- Multiple-channel chemical reactions that generate the active phosphoryl species have been determined. [5]

[5] S. Liang, P. Hemberger, N. M. Neisius, A. Bodi, H. Grutzmacher, J. Levalois-Grutzmacher and S. Gaan, Chemistry-A European Journal 2015, 21, 1073-1080.



Based on pure stoichiometric considerations : Four channels have been determined, why (1) (2) leading to PN are predominant.



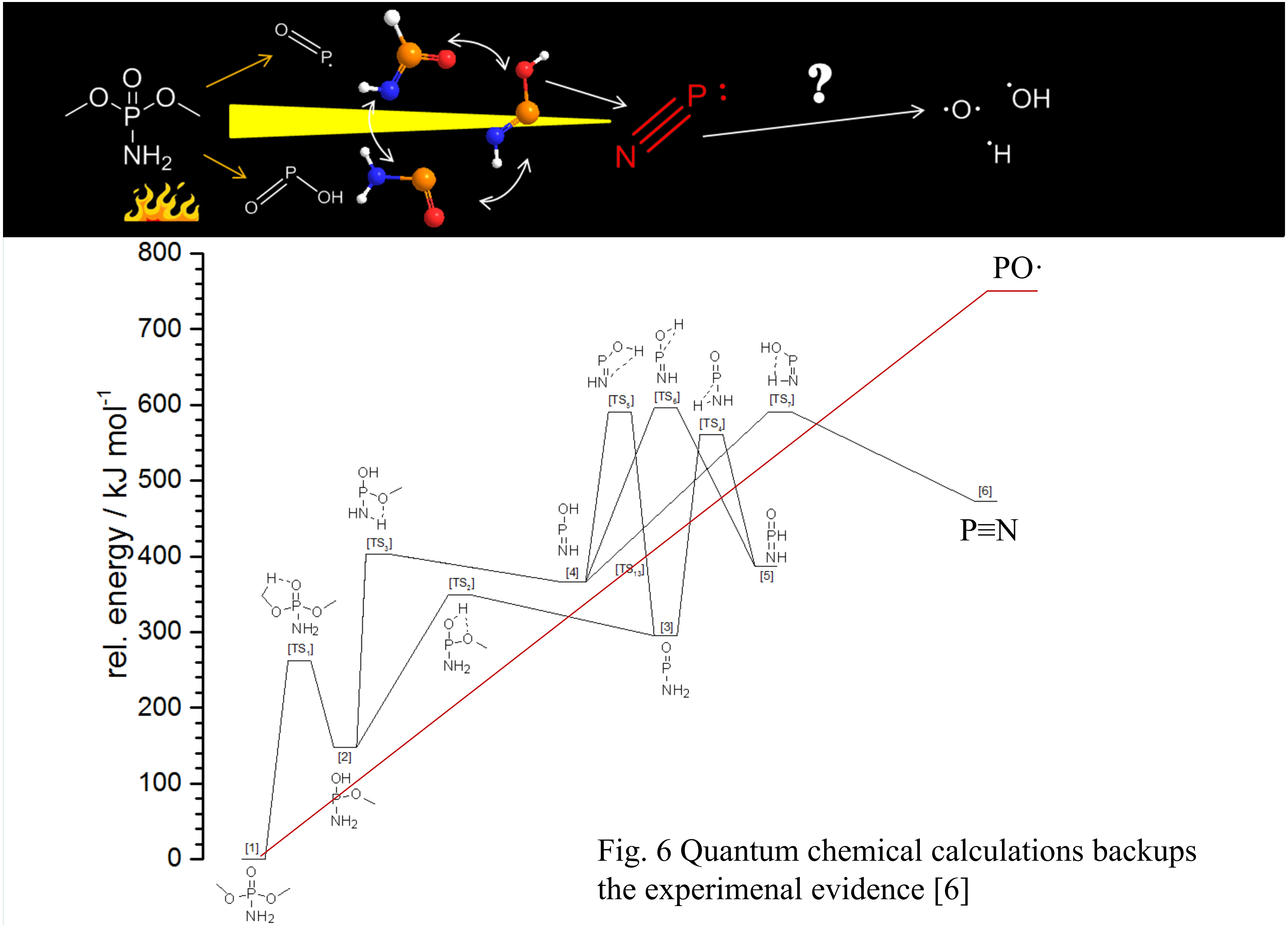
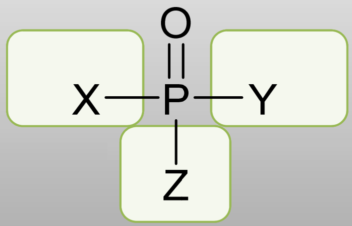
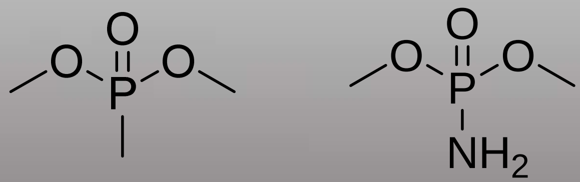


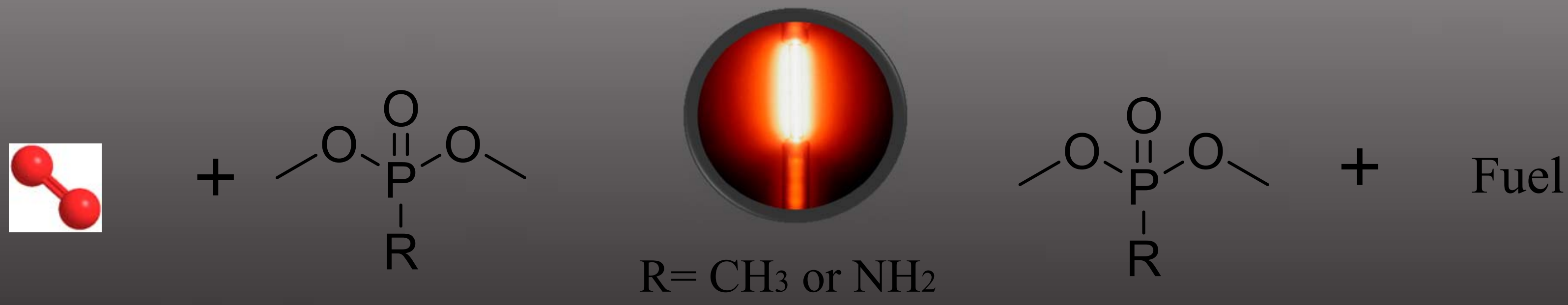
Fig. 6 Quantum chemical calculations backups the experimenal evidence [6]

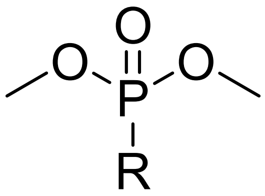
[6] S. Liang, P. Hemberger, N. M., J. Levalois-Grützmacher, H. Grützmacher and S. Gaan, Chemistry-A European Journal 2017, manuscript accepted, in progress.



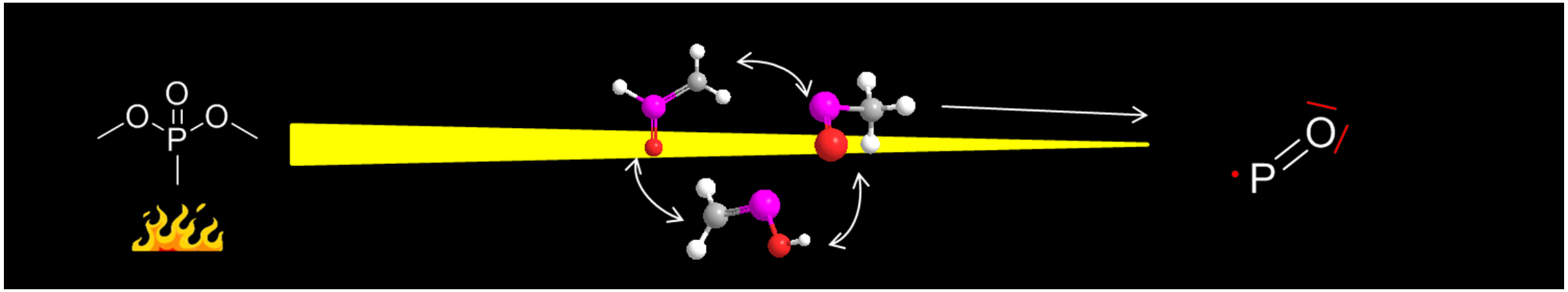
Two phosphorus model compounds

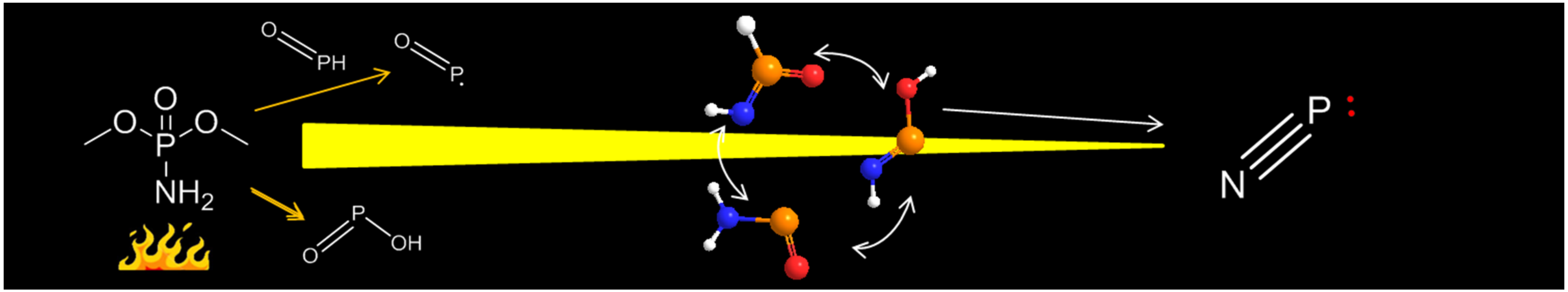


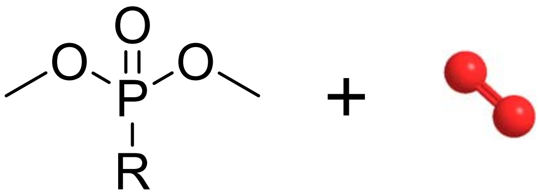


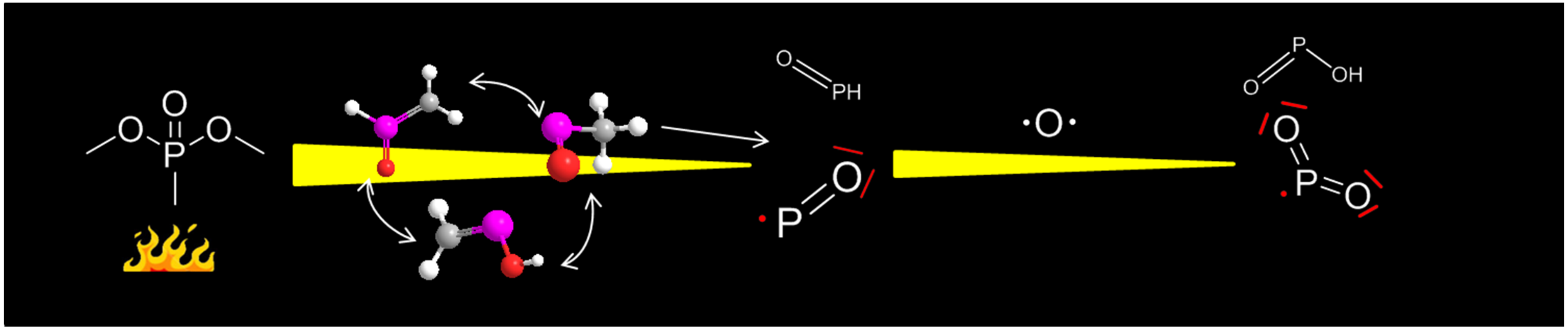


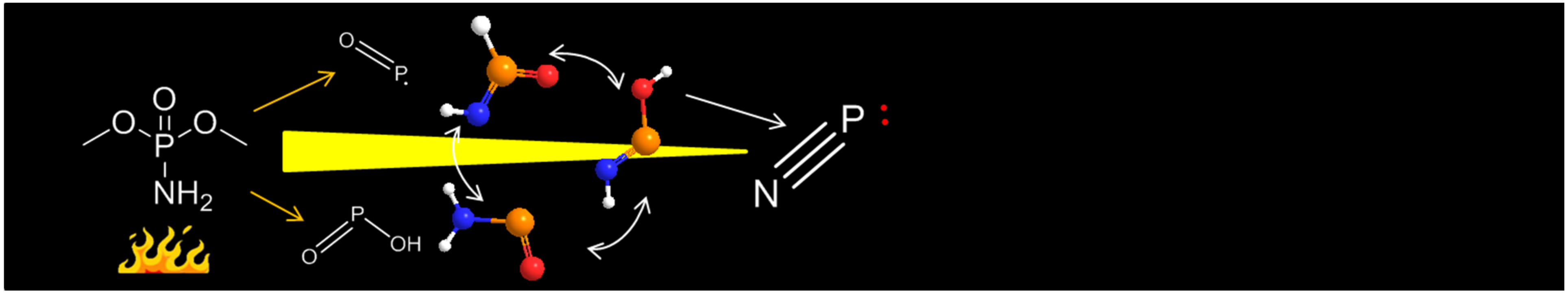
+ Propane







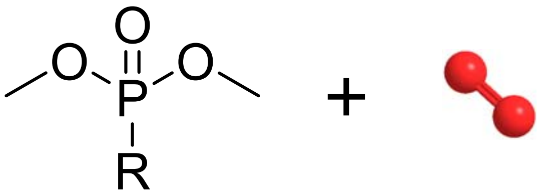


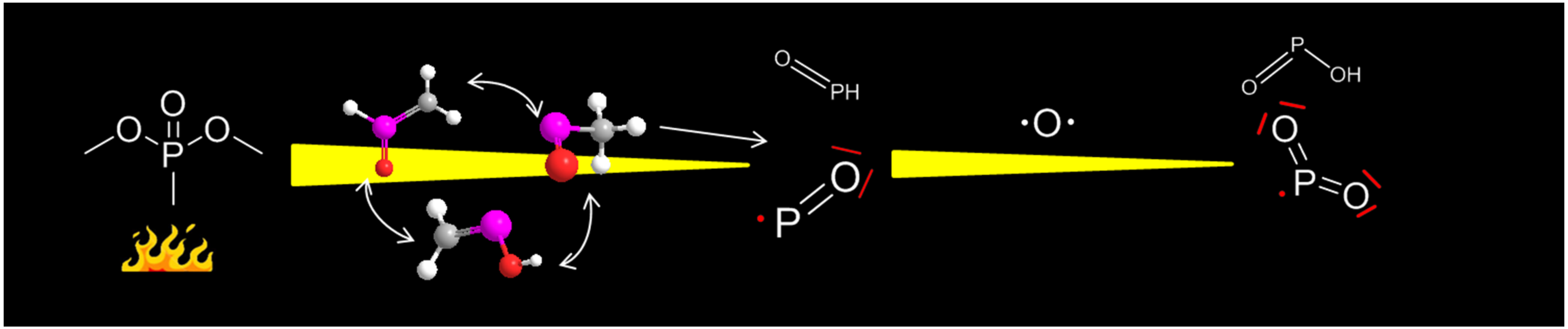


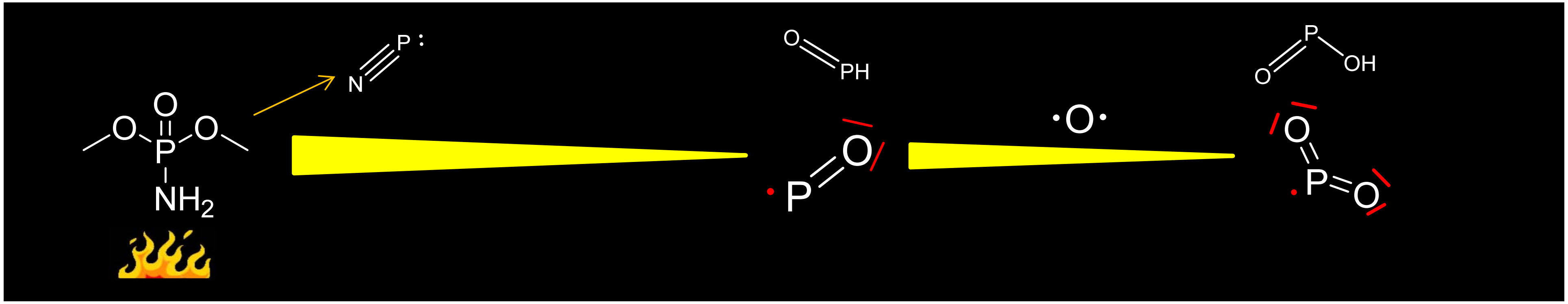
Combustion kick or inhibition:

$*H + *PO_2 \rightarrow HOPO$

$*H + HOPO \rightarrow H_2 + *PO_2$



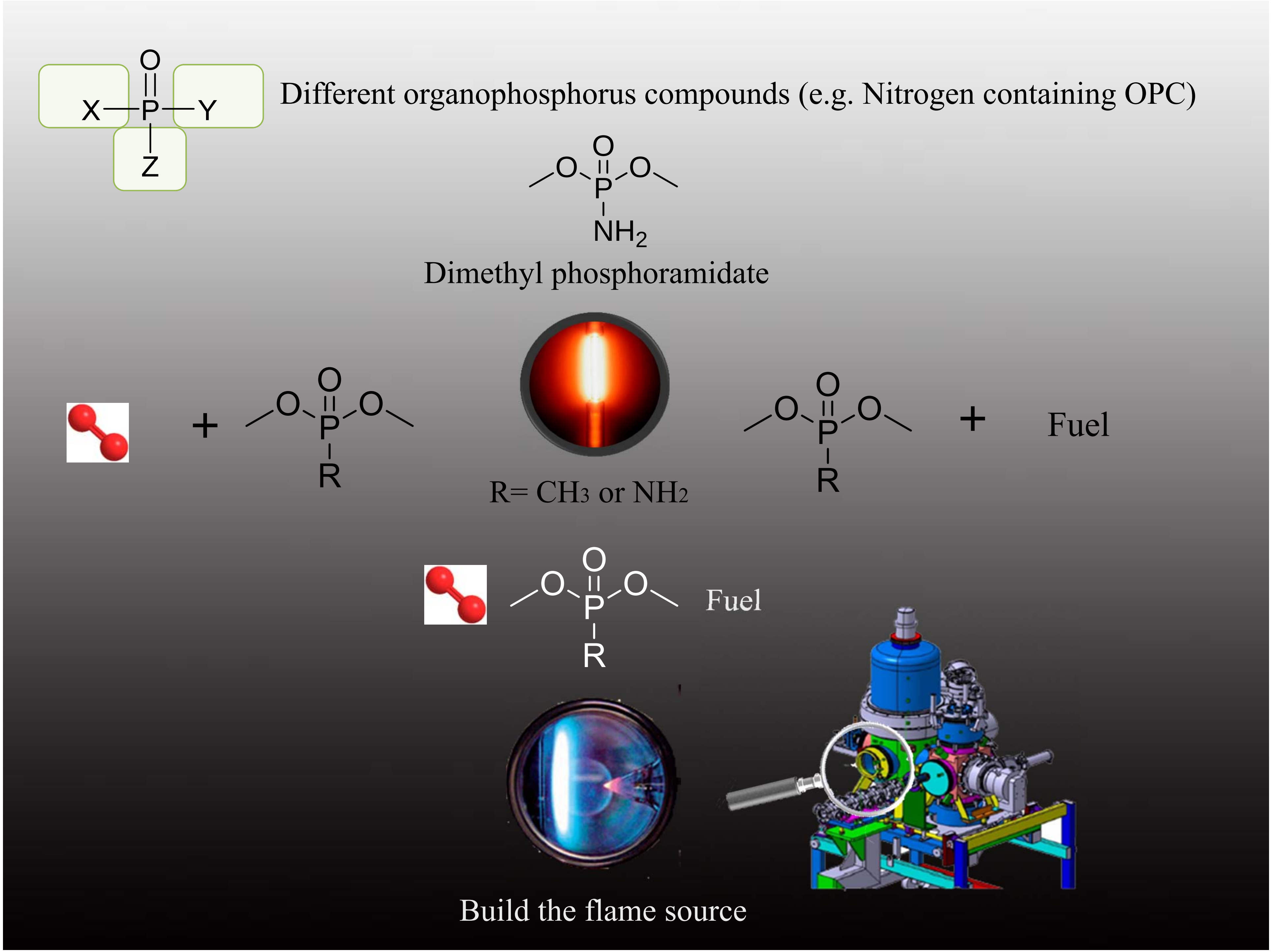




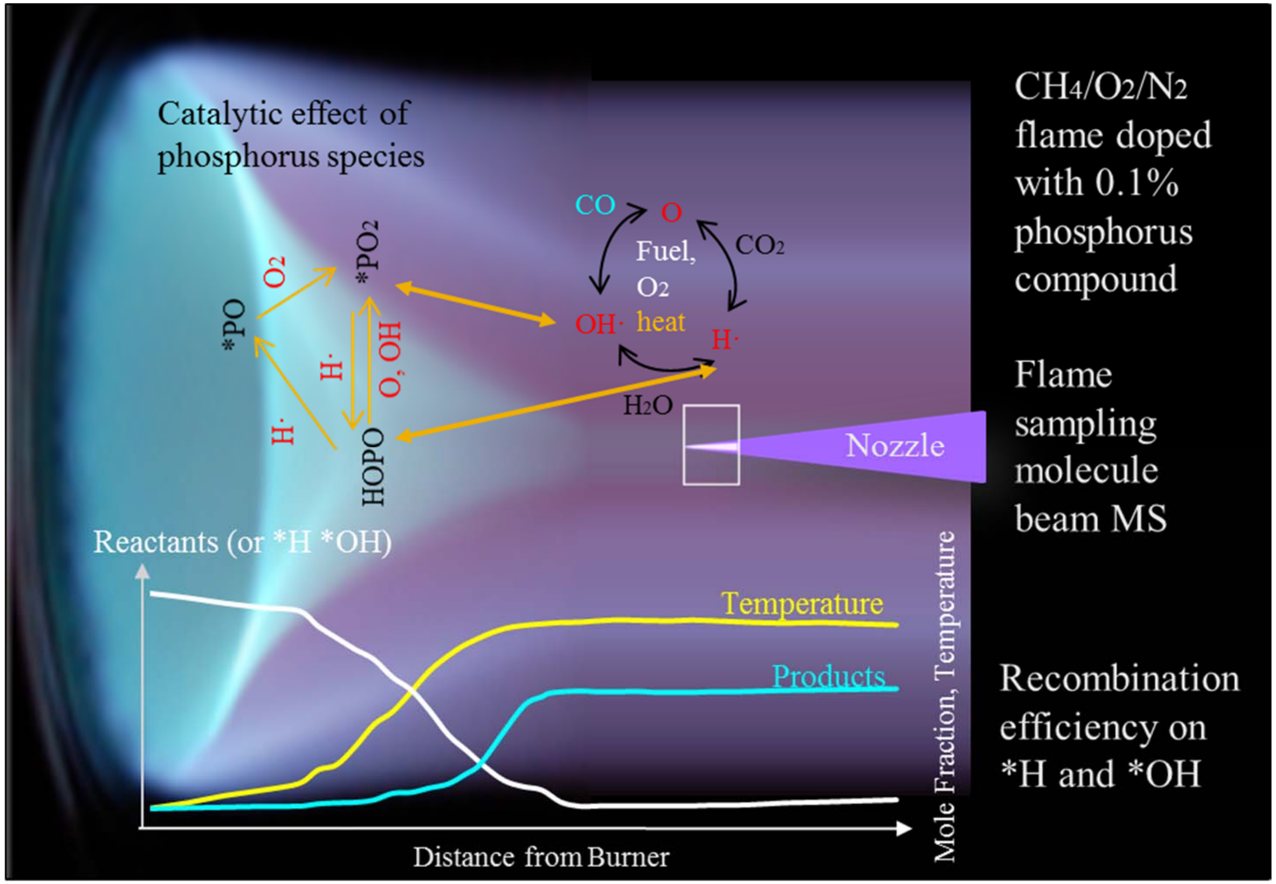
Combustion kick or inhibition:

$*H + *PO_2 \rightarrow HOPO$

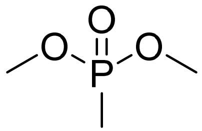
$*H + HOPO \rightarrow H_2 + *PO_2$


Different organophosphorus compounds (e.g. Nitrogen containing OPC)
X
Y
Z
P
O
Dimethyl phosphoramidate
NH_2
+
R
R= CH_3 or NH_2
+
Fuel
Fuel
Build the flame source

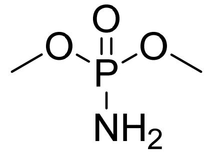
Flame sampling molecular beam mass spectrometry (MBMS)



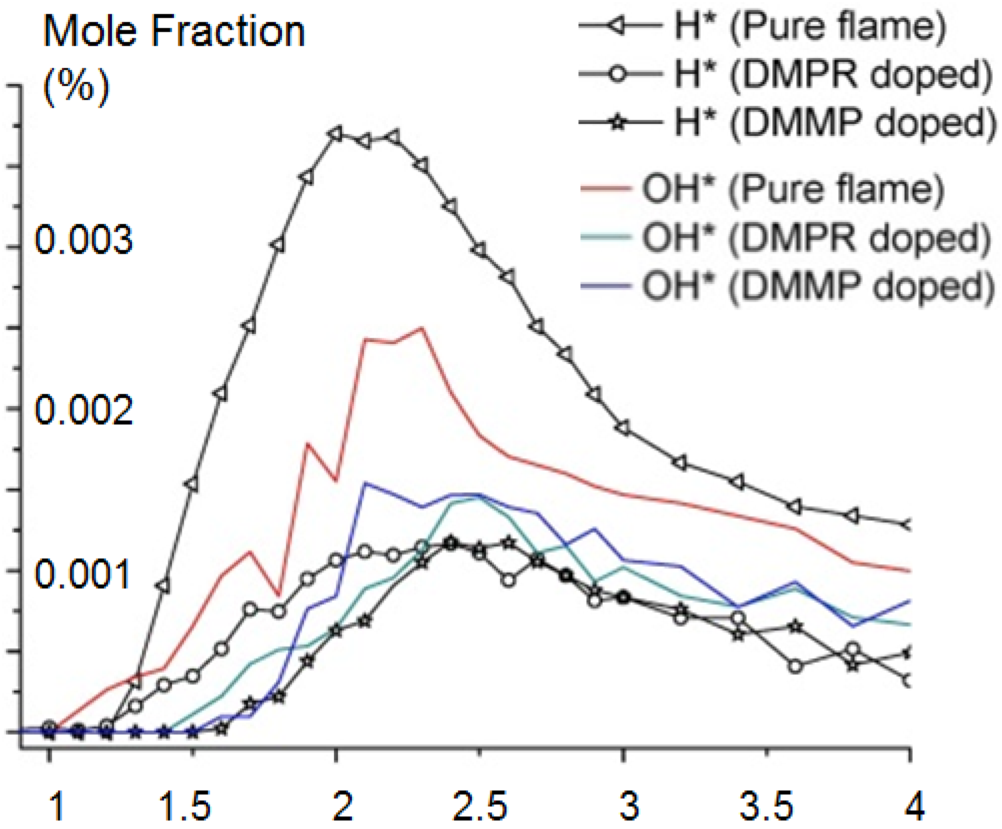
What are the indications of the results under the reactive conditions that are mentioned above?



DMMP



DMPR

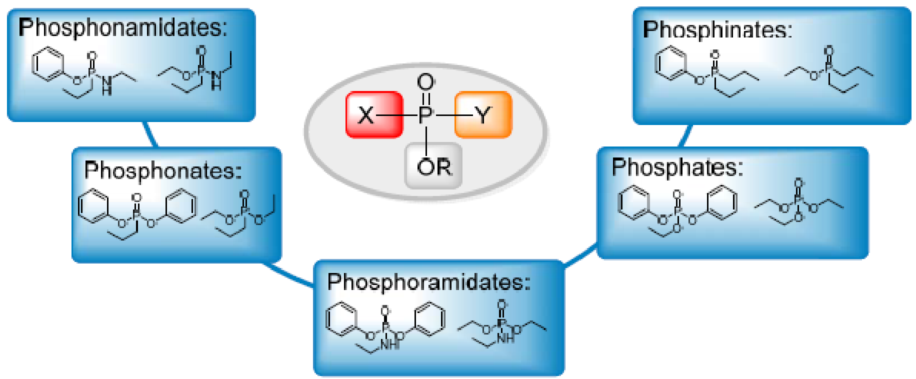


Profiles of concentration of H· and OH· in $CH_4/O_2/N_2$ flame without/with 0.1% DMMP/DMPR

Importance and Impact

(1) Upgrading the instrumentations and furthering the application of iPEPICO technique to disentangle complex reaction mixtures in phosphorus domain

(2) Input on fundamental understandings of phosphorus compound in energy promotion and flame inhibition



(3) Promoting the development of more effective molecule/system which will entail the benefit of energy saving and safety.

(4) Finding the appropriate approach for the incineration/disposal of phosphorus compounds.

Prof. Dr. Hansjörg Grützmacher

Dr. Sabyasachi Gaan

Prof. Dr. Joëlle Levalois-Grützmacher

Dr. Patrick Hemberger

Thank you