KINETIC STUDY OF THE COMBUSTION OF ORGANOPHOSPHORUS COMPOUNDS

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Colloquium: Reaction Kinetics of Combustion

Total word count : 5477

Text: 2408

References: 224

Equations: 245

Tables: 200+2*400=1000

Figures: 400+6*200 = 1600

Abstract : 206

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ABSTRACT

The thermochemistry and kinetics of organophosphorus compounds were studied, with BAC-MP4 estimations as a basis and PM3 semi-empirical estimations for many new compounds. New group additivity values were proposed for enthalpies of formation at 298K, entropies and heat capacities of species involving pentavalent phosphorus bonded to carbon, hydrogen, oxygen, fluorine, nitrogen and sulfur atoms. The kinetic features of unimolecular elimination were investigated by modeling pyrolysis experiments of dimethyl ethyl phosphonate (DEMP), triethyl phosphate (TEP) and di-isopropyl methyl phosphonate (DIMP). Rate constants were proposed for four and six-center eliminations. A new combustion mechanism was developed in a systematic and comprehensive way and involved 41 phosphorus compounds in 202 reactions. All possible intermediates were taken into account. This reaction mechanism was applied to the modeling of dimethyl methyl phosphonate (DMMP) and trimethyl phosphate (TMP) reaction, which are chemical warfare surrogates, in a H_2/O_2 flame. The promoting effect of the agent and the species profiles were correctly reproduced. The decomposition reaction channels were studied, which combine radical reactions and molecular eliminations. The cause of the increase of the reactivity of the flame was attributed to some radical combination cycles leading to an increase of heat release, which enhances the global reaction rate in spite of the radical concentration drop.

INTRODUCTION

Combustion interest in thermochemistry and reaction mechanisms of organophosphorus compounds derives from their roles in incineration of pesticides and chemical warfare agents, fire suppression [1-4], and potential catalytic applications in aircraft turbines [5-6].

Detailed chemical mechanisms must be developed for these applications. Few experimental studies have been reported. In pyrolysis, below 1000 K, Lhomme et al. [7] determined products of the reaction of alkyl phosphates; Durig et al. [8] compared reactivity of six compounds and proposed a decomposition mechanism by unimolecular eliminations. Zegers and Fisher studied thermal decomposition of diethyl methyl phosphonate (DEMP) [9], triethylphosphonate (TEP) [10] and diisopropyl methyl phosphonate (DIMP) [11] in the range 700-900 K. They measured the rate of unimolecular reaction of reactants and proposed mechanisms based on successive molecular eliminations. In combustion conditions, Werner and Cool [12] and Korobeinichev et al. [13] studied the addition of dimethyl methyl phosphonate (DMMP) in a H_2/O_2 flame; both measured phosphorus-containing intermediates and products. Addition of trimethylphosphate (TMP) to a H_2/O_2 flame [14, 16] and a CH_4/O_2 flame [4] was also reported by Korobeinichev et al. with a quantitative determination of the final phosphorus species [4,15-16].

Twarowski proposed a detailed mechanism to explain phosphine addition on the rate of recombination of H and OH [17], including 6 species and 33 reactions. The non-tabulated thermochemical data were evaluated by *ab initio* calculations. An extended version [18] was proposed involving 17 species and 162 reactions, reduced after analysis to 35 reactions. Werner and Cool proposed a 19-step mechanism for combustion of DMMP [12], using Twarowski's data for the small species. Korobeinichev et al. [4] used a mechanism with 34 reactions to describe TMP destruction in flames by radical reactions without molecular elimination.

The present work reports evaluations of thermochemical data as group contributions, allowing estimation of thermochemical properties for numerous new species. A kinetic study of the decomposition mechanism of alkyl phosphate and phosphonate is performed in pyrolysis and in flame to model the effect of organophosphorus additives in combustion and the chemistry controlling incineration of chemical warfare surrogates.

THERMOCHEMISTRY

The thermochemistry of phosphorus compounds is mostly unknown. Without experimental kinetic data available, a postulated kinetic model is strongly dependent on estimation of the heats of formation and entropies of the species. Benson [19] proposed group additivity values for estimation of enthalpies, but not enough to allow characterization of all species involved in a detailed mechanism. We focused on compounds involving a pentavalent phosphorus atom with a double bond with oxygen, the common structure of the species of interest.

Melius performed *ab initio* calculations with the BAC-MP4 method [20], reporting the heat of formation of some alkyl phosphates and alkyl phosphonates and the entropies and heat capacities of six species [21]. Taking these data as a basis, an evaluation of group additivity contributions estimated the thermochemistry of a large number of phosphorus compounds. Six first groups were calculated. Optimization of the group contributions was performed, using as a first guess Benson's values [19] when available or, by analogy, the value of the corresponding group involving (CO) instead of (PO). As many other groups are needed, an evaluation of the properties of new species was done using the UHF/PM3 Hamiltonian and the MOPAC program [22]. Table 1 compares heats of formation calculated with the new group values, BAC-MP4 method, MOPAC and Benson's group values. Despite generally less precise PM3

evaluations, the difference in estimation of enthalpies is less than 10 kcal.mol^{-1} or 6%, below the estimated error given by Melius [20]. For entropy and heat capacity, evaluations done by MOPAC were corrected by the contribution of internal rotors that were not taken into account. The difference with BAC-MP4 calculations is less than 8 cal.mol^{-1} and 8% for entropy, and appears related to groups bonded to the (PO) group. Correction factors were determined and applied to subsequent calculations. Corrections used are, for each substituent, -1.5 cal.mol^{-1} for OH, -1 cal.mol^{-1} for CH_3 or NH_2, -2 cal.mol^{-1} for C_2H_5, -2.5 cal.mol^{-1} for OCH_3, +3.3 cal.mol^{-1} for H, F or two of them.

Nineteen other group contributions are based on evaluation of thermochemical data of new phosphorus compounds by MOPAC as described, involving C, H, O, F, N, S and C≡N substituents. When the heat of formation had been calculated by Melius [20], the BAC-MP4 value was preferred for the determination of the enthalpy. This case occurred for the following groups: PO-$(H)_2$(O), PO-(H)$(O)_2$, PO-(C)$(F)_2$, PO-(C)(F)(O), PO-(F)$(O)_2$, PO-(N)$(O)_2$, C-(C)$(H)_2$(PO). Table 2 summarizes all proposed group values.

KINETIC MODELING

Combustion chemistry of organophosphorus compounds can be postulated by analogy with better-known carbonated species. Radical reactions and molecular eliminations must be considered.

Unimolecular decompositions

Two kinds of molecular decomposition seem to play a role in the degradation of alkyl phosphate or phosphonates. A six-center concerted reaction leads to elimination of an alkyl group, producing an alkene and OH group bonded to P. The reaction occurs by formation of a

cyclic transition state where an H-atom of the alkyl group is abstracted by the O-atom of the (P=O) [9,19]. The four-center reaction involves abstraction of H atoms from an OH substituent by an O-atom that leads to the elimination of alcohol or water and formation of a PO_2 group [9,19].

Zegers and Fisher measured rates of the six-center elimination for DEMP [9], TEP [10] and DIMP [11] by following decay of the reactant in pyrolysis between 700K and 900K. Rates are in good agreement with ester decomposition into acid and alkene involving the same kind of transition state [11]. However, measurements of ester decomposition show that the pre-exponential factor *A* for such a six-member transition state is between 3.10^{12} and 10^{13} s^{-1} [11,19]. We adopt the value of 10^{13} s^{-1} for DEMP decomposition, considering six abstractable H-atoms instead of three. Because of the larger H-atom number, *A* should be about two times higher for the reaction of TEP and DIMP. Activation energies were corrected to fit these *A*-factors to experimentally measured rate constants at 800K. In the case of TEP, *A* is higher to keep the same activation energy as for DEMP. The rates are given in Table 3.

No experimental measurements have been reported for the four-center decomposition. To estimate these rates, experimental results of Zegers and Fisher were modeled. Based on the analysis of reaction products, alkene and alcohol, we assume, like these authors, that no radical reaction occurs with the parent compound, but only successive six-center and four-center eliminations. The postulated mechanism is given in Table 3. Rates of the six-center decomposition of the intermediates are the same as the reactant decomposition after a correction of the *A*-factor for taking into account the H-atom number. Rates of the four–center eliminations are then adjusted to reproduce experimentally observed formation of alcohol and alkene.

Experimental results [9-11] were obtained in an atmospheric pressure flow reactor, with the reactant diluted in nitrogen. Measured products are ethylene and ethanol in the reaction of

DEMP and TEP, and propene and *i*-propanol in the reaction of DIMP. Because heterogeneous effects change the ratio between the products [9-11], the initial load used for the calculations is the amount extrapolated to t = 0 at the lower temperature studied. This assumption supposes that heterogeneous reactions are independent of temperature and play a role in the entrance section of the flow reactor but may be neglected downstream. For DIMP, the load used is exactly the initial one, but the start of the reaction is shifted by 10 ms.

Pre-exponential factors for the four-center eliminations are chosen to be in the same order as corresponding reactions reported with carbonated compounds [19], respectively, 2.5×10^{13}, 3.5×10^{13} and 5×10^{13} s^{-1} for formation of ethanol, *i*-propanol and water. With such values, the activation energy should be near the enthalpy of reaction to be able to reproduce the experimental results, a situation very different from other known reactions involving the same kind of transition state [18]. The activation energy of the reverse reaction, a molecular addition of water or alcohol on a PO_2 function, is then very low, and should be below 2 $kcal.mol^{-1}$.

Figure 1 compares the calculated ratios of alcohol and alkene to the experimental ones for the three reactants. For the highest conversions, obtained for long residence time, the alcohol production drops off in agreement with experimental results. This is due to a shift in the equilibrium of the four-center elimination reactions, which are in partial equilibrium at high conversion. This shift favors the reverse reaction of addition of alcohol:

$$CH_3PO_2 + C_2H_5OH \leftrightarrow PO(OH)(OEt)(CH_3)$$

as are phosphonates consumed:

$$PO(OH)(OEt)(CH_3) \leftrightarrow PO(OH)_2(CH_3) + C_2H_4$$

Figures 2 shows reactants and carbonated products profiles for the pyrolysis of DIMP. The most important phosphorus product is then CH_3PO_2 which is in equilibrium with water and *i*-propanol.

Combustion model

A mechanism has been built to reproduce combustion of DMMP and TMP. It includes reaction types usually considered in the combustion of hydrocarbons and the possible molecular eliminations. Major molecular intermediates taken into account are $PO(OH)(OCH_3)_2$, $PO(OH)(CH_3)(OCH_3)$, $PO(OH)_2(OCH_3)$, $PO(OH)_2(CH_3)$, $PO(OH)_3$, CH_3PO, CH_3OPO, CH_3PO_2 and CH_3OPO_2. These compounds react by molecular elimination, bond-scission, H-abstraction by O_2 or a free radical, and addition of H or OH to the P=O double bond. The radicals produced then react by combination with small free radicals or by decomposition involving a bond breaking via β-scission. The ultimate products are HOPO, $HOPO_2$, HPO, HPO_2, PO, PO_2, and PO_3. For these species, all unimolecular and bimolecular possible reactions are written by considering also reactions with H, O, OH, HO_2, H_2O and CH_3. The complete mechanism consists of 41 different phosphorus species involving 202 reactions. The kinetic data were estimated by analogy with reactions of carbon or nitrogen containing species and by thermochemical considerations. The molecular elimination rates were evaluated by analogy with ones determined in the pyrolysis study. Rates of H-abstraction were calculated with the Evans–Polanyi correlation proposed by Dean and Bozzelli [23]. The addition of H and OH to P=O were estimated, respectively, at $5.0\times10^{12}.\exp(-5000/RT)$ $cm^3.mol^{-1}.s^{-1}$ and $1.4\times10^{12}.\exp(-2000/RT)$ $cm^3.mol^{-1}.s^{-1}$ by analogy with the addition to a C=O bond.

The mechanism used for modeling the combustion of oxygenated and carbonated species is derived from a mechanism of combustion of dimethylether [24]. We retained species containing two or less C-atoms and their associated reactions giving a sub-mechanism of 51 species and 263 reactions.

This mechanism has been used to model the combustion of DMMP and TMP doped $H_2/O_2/Ar$ stabilized premixed stoichiometric flames in the experimental conditions of

Korobeinichev [13,16]. The calculations were performed with the PREMIX [25] code. Figure 3 compares computed and experimental temperature profiles of the flame with and without the addition of 0.2% of DMMP [13]. The increased heat release when DMMP is added is well reproduced by the model. Figure 4 compares the profiles of reactants and water obtained with and without the addition of TMP at the experimental conditions of [16]. For both DMMP and TMP, the promoting effect of the phosphorus additive is well reproduced by the model. The reaction mechanism is available from the authors or on the Web at http://www-cms.llnl.gov/combustion/combustion_home.html.

The additives are quickly consumed in the first stage of the flame. Intermediate alkyl phosphates and phosphonates are produced close to the burner by addition of H to the P=O bond followed by decomposition.

$$PO(CH_3)(OCH_3)_2 + H \rightarrow PO(OH)(CH_3)(OCH_3) + CH_3$$

Figure 5 shows computed profiles of DMMP and phosphorus intermediates at the experimental conditions of [13]. These compounds react mainly by H-atom addition or a 4-center elimination

$$PO(OH)(CH_3)(OCH_3) + H \rightarrow PO(OH)_2(CH_3) + CH_3$$

$$PO(OH)(CH_3)(OCH_3) \rightarrow CH_3PO_2 + CH_3OH$$

When temperature increases, the H-abstraction channel becomes predominant and leads to successive decompositions:

$$PO(CH_3)(OCH_3)_2 + H \rightarrow PO(CH_3)(OCH_3)(OCH_2) + H_2$$

$$PO(CH_3)(OCH_3)(OCH_2) \rightarrow PO(CH_3)(OCH_3) + CH_2O$$

$$PO(CH_3)(OCH_3) \rightarrow CH_3OPO + CH_3$$

By addition of H-radical, species as CH_3PO_2 or CH_3OPO produce small oxides. These are orthophosphoric acid, HOPO, $HOPO_2$ and radicals PO and PO_2. Figures 6 and 7 compare experimental and calculated profiles of these species in the flame doped with TMP [16]. Near the

burner, orthophosphoric acid is most stable, decomposing into $HOPO_2$ and water when the temperature increases. HOPO reacts mainly by H-abstraction giving PO_2, while H adds to $HOPO_2$ to give $PO(OH)_2$ radical; which combines with other radicals at lower temperatures or decomposing into HOPO and OH at higher temperatures.

The promoting effect of the phosphorus additive comes from enhanced heat release closer to the burner from exothermic recombination reactions induced by the phosphorus species. In other conditions such as methane flames [1-4], the drop of radical concentration in the flame caused by recombination leads to an inhibiting effect; in the case of H_2/O_2 flame where H-radicals are very abundant and react mainly with oxygen, the higher temperature allows a strong acceleration of the combustion by the way of the very sensitive branching reaction:

$$H + O_2 \rightarrow OH + O$$

with a high activation energy of 16.5 kmal.mol^{-1}.

The sensitivity analysis shows that in the very beginning of the H_2/O_2 doped flame, a termination cycle appears with H-abstractions on the DMMP or TMP followed by combination of the produced radical or the radicals produced after a decomposition. In the case of DMMP:

$$PO(CH_3)(OCH_3)(OCH_2) + H \rightarrow PO(CH_3)(OCH_3)_2$$

Later, the major termination effect comes from the cycle already proposed by Twarowski [18] that involves PO_2:

$$PO_2 + H \rightarrow HOPO$$

$$HOPO + X \rightarrow PO_2 + HX \qquad X = H, O \text{ or } OH$$

Despite the loss of H-atoms, which react otherwise with O_2 and produce chain branching, these termination cycles have a promoting effect because of the high exothermicity of H_2 or water formation. The present modeling results indicate that formation of the more stable $HOPO_2$,

which reduces the termination cycles, has an inhibiting effect by reducing the amount of PO_2 radicals:

$$PO_2 + OH \rightarrow HOPO_2$$

In contrast, the consumption of this specie to give HOPO increases the global reaction rate:

$$HOPO_2 + H \rightarrow PO(OH)_2$$

$$PO(OH)_2 \rightarrow HOPO + OH$$

CONCLUSION

An evaluation of thermodynamical properties of organophosphorus compounds was performed by proposing some incremental group values for enthalpy, entropy and heat capacity. The 25 groups involving C, H, N, O, F, S and CN bonded to PO allow prediction of properties of many species, for which no data were currently available, with reasonable accuracy.

Modeling of pyrolysis of DEMP, TEP and DIMP permitted evaluation of the rate constants of some molecular eliminations whose importance was previously not easy to estimate under combustion conditions. A large combustion mechanism developed for DMMP and TMP was validated against experimental results obtained in doped H_2/O_2 flames. This new mechanism, taking into account all possible intermediates, is more complete and comprehensive than previous ones. The model allows then the prediction of decomposition routes and the products formed, which are interesting in incineration of chemical waste. An explanation of the promoting effect on the studied flames is proposed and evaluated for each of the different phosphorus oxides.

ACKNOWLEDGMENTS

The authors thank V. Babushok for providing thermochemical data and E. Zegers and E. Fisher for their experimental data and insights. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under the contract No. W-7405-ENG-48.

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FIGURE CAPTIONS

Figure 1: Ratio of alcohol and alkene amount formed in the pyrolysis of DEMP [9], TEP [10], and DIMP [11] in flow reactor under 1 atm. Curves are model predictions.

Figure 2: Profiles of species in the pyrolysis of DIMP at 799 K in flow reactor under 1 atm [11]. Curves are model predictions.

Figure 3: Experimental and computed profiles of the temperature in the stoichiometric premixed $H_2/O_2/Ar$ flame [13] (mole fraction: 0.26/0.13/0.61), doped with 0.2% vol. of DMMP. P= 80 Torr.

Figure 4: Experimental and computed profiles of H_2, O_2 and H_2O in the stoichiometric premixed $H_2/O_2/Ar$ flame [16] (mole fraction: 0.26/0.13/0.61) with and without the addition of 0.2% vol. of TMP. P = 47 Torr. Curves are model predictions. Full symbols and curves refer to the doped flame, open symbols and dashed curves refer to undoped flame.

Figure 5: Computed profiles of DMMP and intermediate phosphorus species in the stoichiometric premixed $H_2/O_2/Ar$ flame [13] (mole fraction: 0.26/0.13/0.61), doped with 0.2% vol. of DMMP. P= 80 Torr.

Figure 6: Experimental and computed profiles of HOPO, $HOPO_2$ and orthophosphoric acid in the stoichiometric premixed $H_2/O_2/Ar$ flame [16] (mole fraction: 0.26/0.13/0.61) doped with 0.2% vol. of TMP. P = 47 Torr. Curves are model predictions.

Figure 7: Experimental and computed profiles of PO and PO_2 in the stoichiometric premixed $H_2/O_2/Ar$ flame [16] (mole fraction: 0.26/0.13/0.61) doped with 0.2% vol. of TMP. P = 47 Torr. Curves are model predictions.

Table 1 : Standard enthalpy of formation of selected compounds (in kcal.mol^{-1}).

Species	This study	BAC-MP4 [21]	PM3 calc.	Benson [19]
$PO(CH_3)(OCH_3)_2$	-196.4	-196.4	-189.2	-211.1
$PO(H)(CH_3)(OCH_3)$	-131.1	-131.5	-134.1	—
$PO(OH)(CH_3)(OCH_3)$	-204.4	-206.7	-195.6	-225.4
$PO(OH)(OCH_3)_2$	-255.1	-255.6	-250.6	-271.2
$PO(OH)_3$	-271.1	-272.3	-270.2	-299.6
$PO(OH)_2(CH_3)$	-212.4	-210.9	-209.1	-239.6

Table 2 : Group contributions for organophosphorus compounds at 298 K.

Group	$\Delta H_f°$ kcal.mol^{-1}	S° cal.K^{-1}.mol^{-1}	$C_p°$ cal.K^{-1}.mol^{-1}
PO-(C)(H)(O)	-74.3	23.1	9.5
PO-(C)$(O)_2$	-92.7	0.3	9.3
PO-$(O)_3$	-106.4	-0.2	9.1
PO-$(H)_2$(O)	-69.1	39.7	9.5
PO-(H)$(O)_2$	-91.1	19.2	9.3
PO-(C)(F)(H)	-138.0	49.3	12.1
PO-(C)$(F)_2$	-215.1	55.3	16.5
PO-(C)(F)(O)	-161.6	24.7	11.4
PO-(F)$(O)_2$	-173.1	20.6	12.1
PO-(F)(H)(O)	-157.5	47.7	12.6
PO-(CN)(C)(O)	-46.3	30.9	15.4
PO-(C)(N)(O)	-70.3	4.8	9.9
PO-(N)$(O)_2$	-94.5	-0.5	9.6
PO-(CN)(N)(O)	-42.0	33.7	17.1
PO-(C)(O)(S)	-63.9	1.6	6.9
C-$(H)_3$(PO)[a]	-9.95	28.1	6.19
C-(C)$(H)_2$(PO)	-5.2	3.0	3.9
O-(H)(PO)	-54.9	27.9	4.7
O-(C)(PO)	-36.8	8.2	2.8
O-$(PO)_2$	-56.4	1.8	6.2
N-$(H)_2$(PO)[b]	-14.9	24.69	4.07
N-(C)(H)(PO)	-3.2	4.4	3.1
N-$(C)_2$(PO)	8.6	-17.3	4.5
S-(H)(PO)[c]	-1.4	31.2	7.63
S-(C)(PO)	6.4	11.3	5.4

[a] C-$(H)_3$(PO) ≡ C-$(H)_3$(CO) assigned for $C_p°$.

[b] N-$(H)_2$(PO) ≡ N-$(H)_2$(CO) assigned.

[c] S-(H)(PO) ≡ S-(H)(CO) assigned.

Table 3 : Pyrolysis mechanism of DEMP, DIMP and TEP

Reaction	A	b	E
DEMP ↔ $PO(OH)(OEt)(CH_3) + C_2H_4$	1×10^{13}	0	45300[a]
$PO(OH)(OEt)(CH_3)$ ↔ $PO(OH)_2(CH_3) + C_2H_4$	5×10^{12}	0	45300
$PO(OH)(OEt)(CH_3)$ ↔ $CH_3PO_2 + C_2H_5OH$	2.5×10^{13}	0	44000
$PO(OH)_2(CH_3)$ ↔ $CH_3PO_2 + H_2O$	5×10^{13}	0	39000
DIMP ↔ $PO(OH)(OiPr)(CH_3) + C_3H_6$	2×10^{13}	0	41200[a]
$PO(OH)(OiPr)(CH_3)$ ↔ $PO(OH)_2(CH_3) + C_3H_6$	1×10^{13}	0	41200
$PO(OH)(OiPr)(CH_3)$ ↔ $CH_3PO_2 + C_3H_7OH$	3.5×10^{13}	0	43000
TEP ↔ $PO(OH)(OEt)_2 + C_2H_4$	2.8×10^{13}	0	45300[a]
$PO(OH)(OEt)_2$ ↔ $PO(OH)_2(OEt) + C_2H_4$	1.9×10^{13}	0	45300
$PO(OH)(OEt)_2$ ↔ $C_2H_5OPO_2 + C_2H_5OH$	2.5×10^{13}	0	44000
$PO(OH)_2(OEt)$ ↔ $PO(OH)_3 + C_2H_4$	9.6×10^{12}	0	45300
$PO(OH)_2(OEt)$ ↔ $HOPO_2 + C_2H_5OH$	2.5×10^{13}	0	44000
$C_2H_5OPO_2$ ↔ $HOPO_2 + C_2H_4$	1.9×10^{13}	0	45300
$PO(OH)_2(OEt)$ ↔ $C_2H_5OPO_2 + H_2O$	5×10^{13}	0	45000
$PO(OH)_3$ ↔ $HOPO_2 + H_2O$	1.5×10^{14}	0	46000

[a] Calculated from [9-11], see text. Units are mol, cm^3, s, K and $cal.mol^{-1}$.

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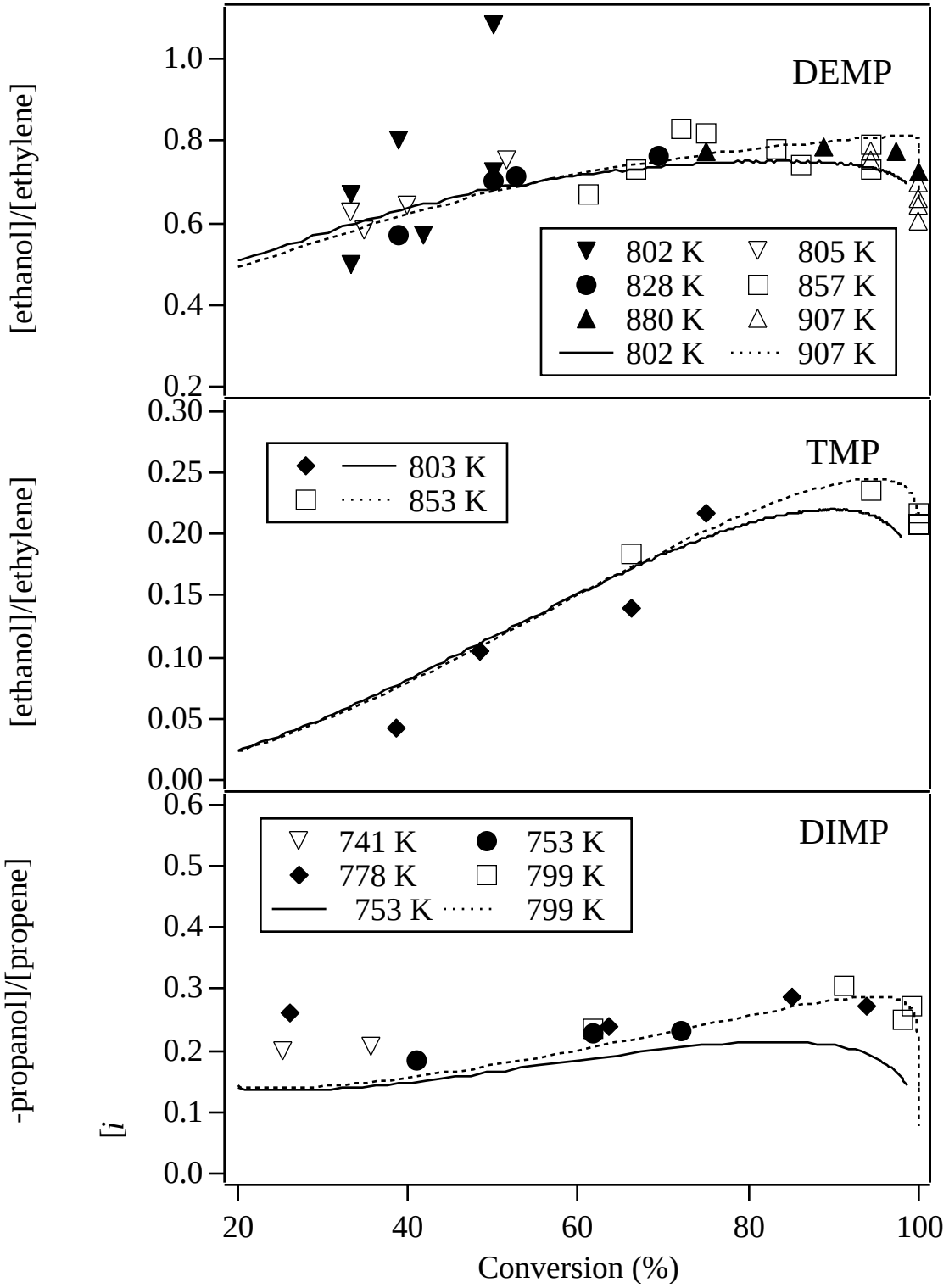
DEMP
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805 K
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857 K
880 K
907 K
802 K
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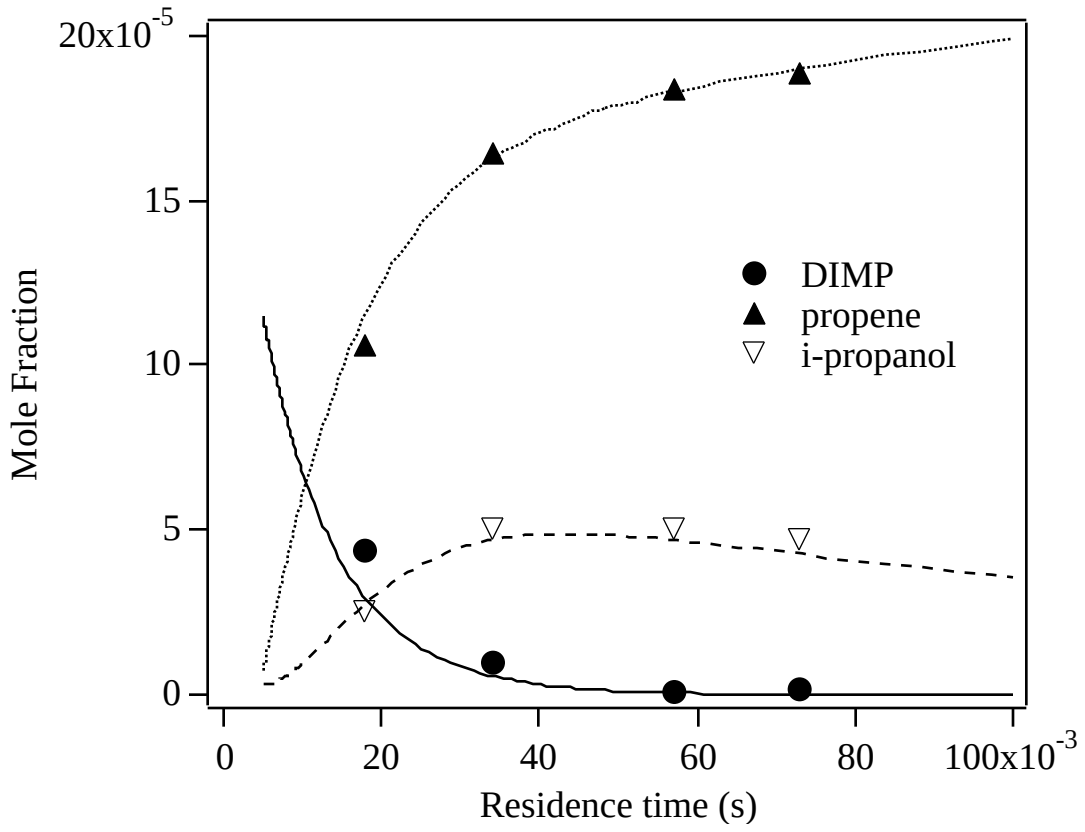
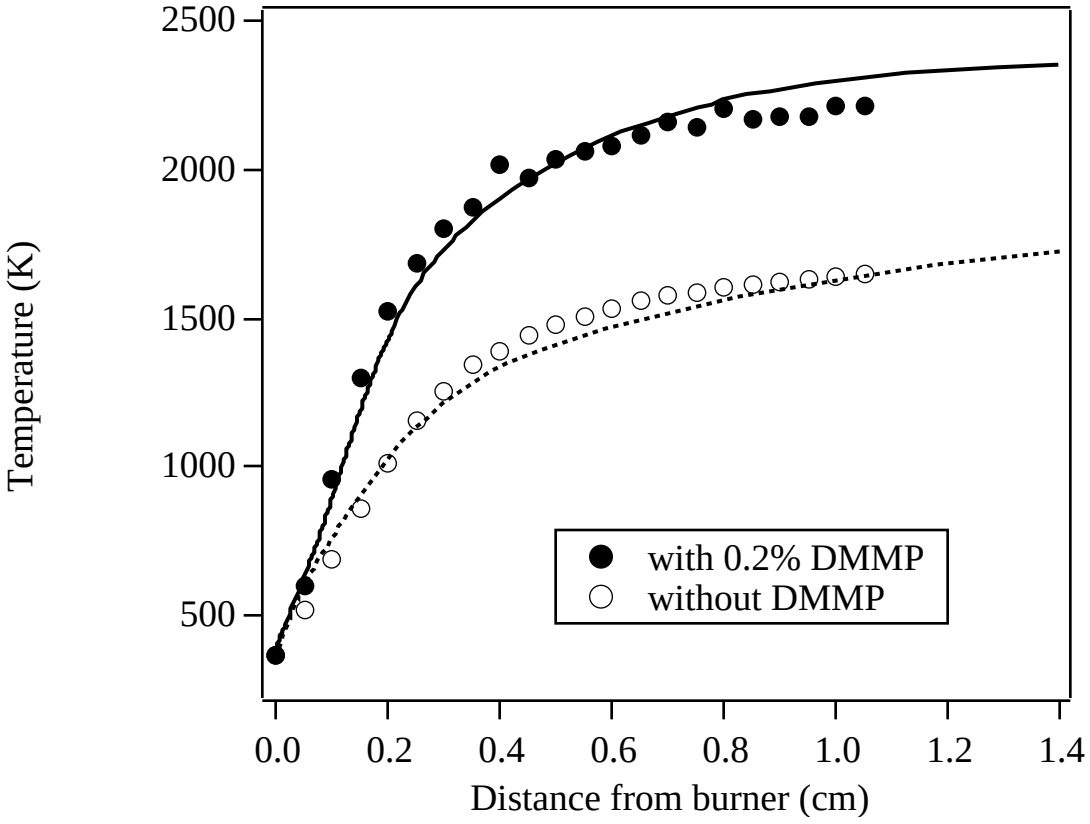
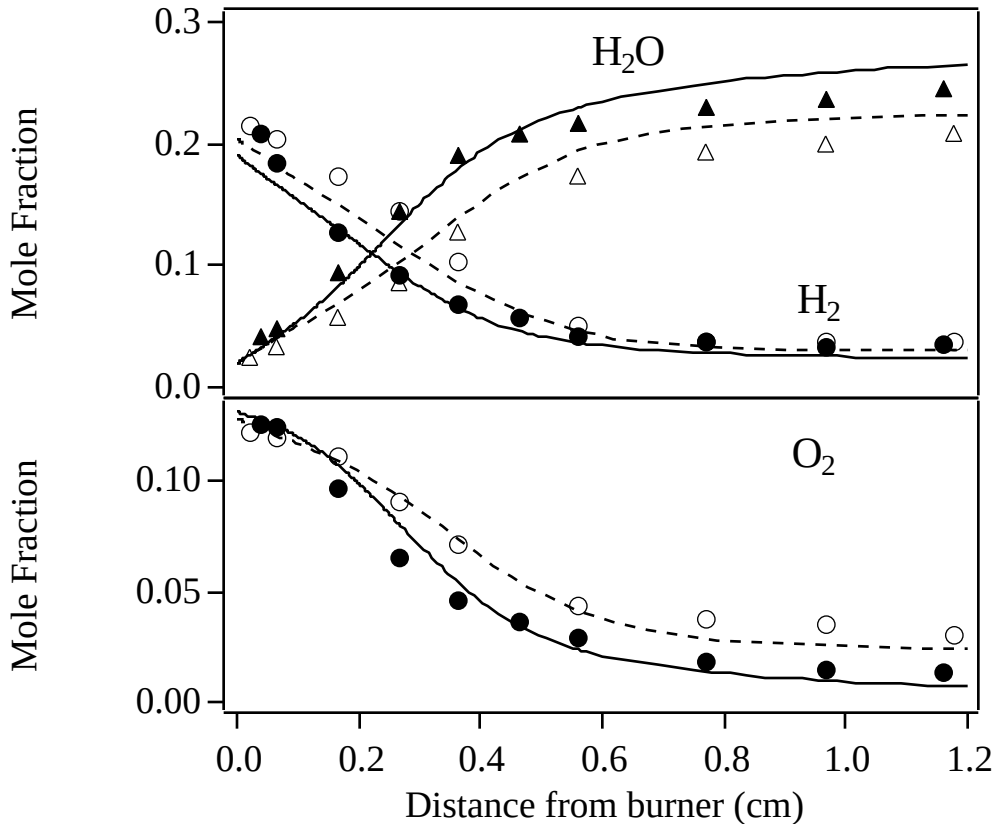
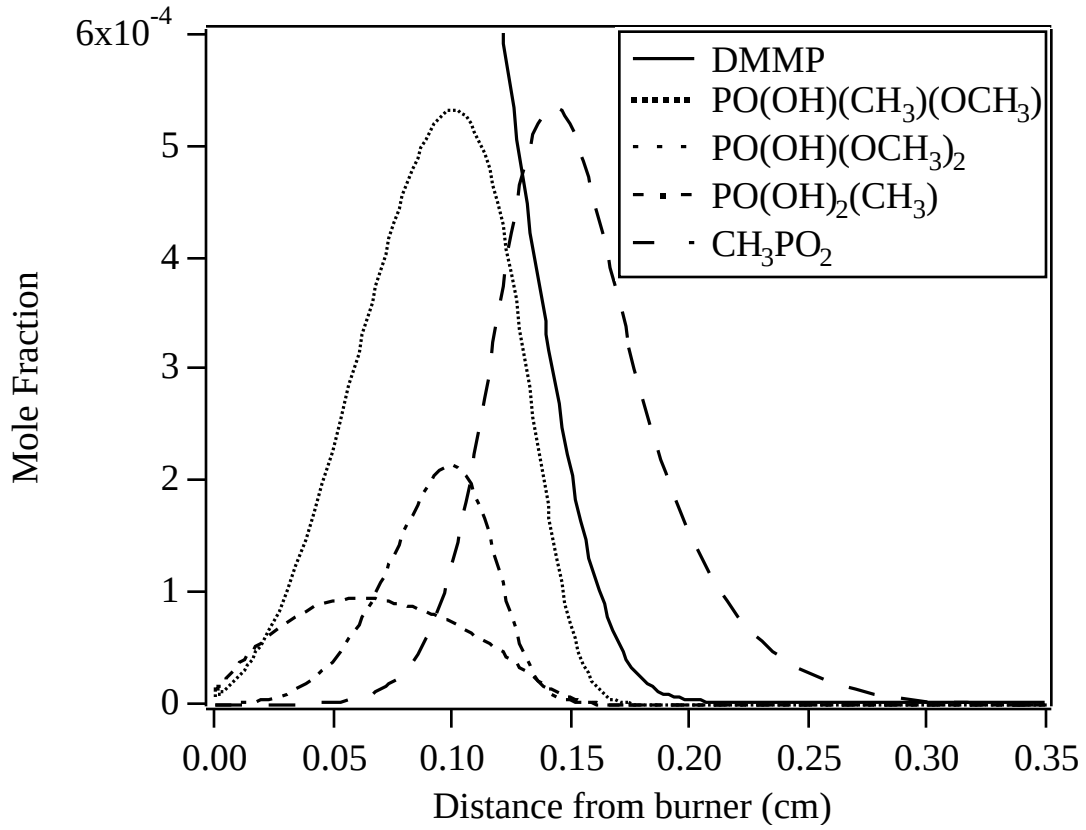
[ethanol]/[ethylene]
TMP
803 K
853 K
[ethanol]/[ethylene]
DIMP
741 K
753 K
778 K
799 K
753 K
799 K
[i-propanol]/[propene]
Conversion (%)

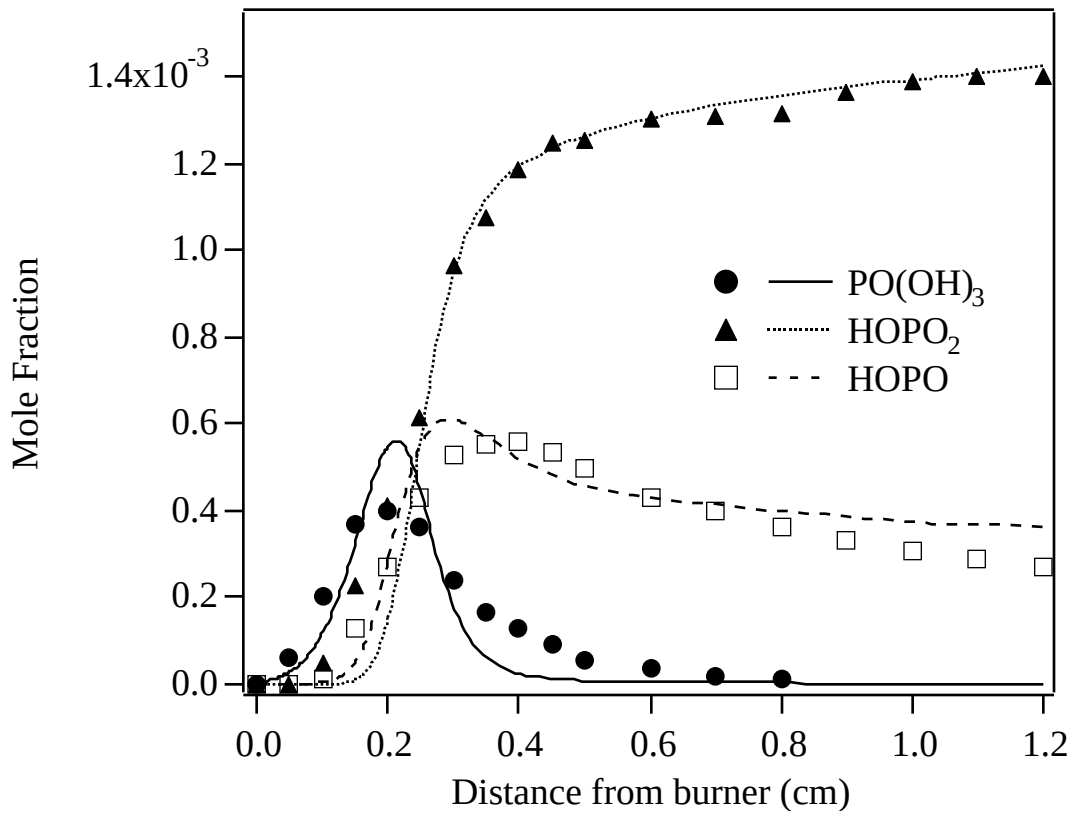
2

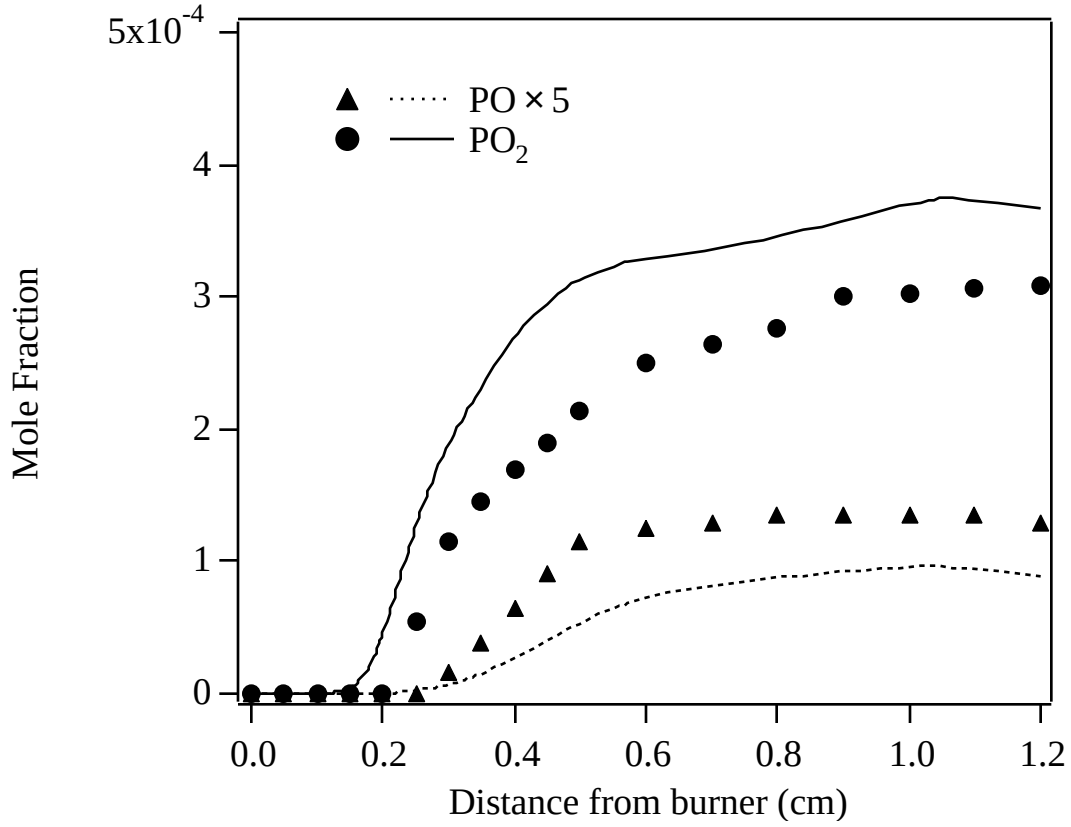

20x10-5
15
10
5
0
Mole Fraction
0
20
40
60
80
100x10-3
Residence time (s)
DIMP
propene
i-propanol


2500
2000
1500
1000
500
Temperature (K)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Distance from burner (cm)
with 0.2% DMMP
without DMMP


0.3
0.2
0.1
0.0
Mole Fraction
H_2O
H_2
0.10
0.05
0.00
Mole Fraction
O_2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Distance from burner (cm)


6x10-4
5
4
3
2
1
0
Mole Fraction
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
Distance from burner (cm)
DMMP
PO(OH)(CH3)(OCH3)
PO(OH)(OCH3)2
PO(OH)2(CH3)
CH3PO2


1.4x10-3
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Mole Fraction
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Distance from burner (cm)
PO(OH)3
HOPO2
HOPO


5x10-4
4
3
2
1
0
Mole Fraction
PO × 5
PO2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Distance from burner (cm)