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KINETIC STUDY OF THE COMBUSTION OF ORGANOPHOSPHORUS COMPOUNDS

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The thermochemistry and kinetics of organophosphorus compounds were studied, with BAC-MP4 method estimations as a basis and PM3 semi-empirical estimations for many new compounds. New group additivity values were proposed for enthalpies of formation at 298 K, and 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 H_2/O_2 flames doped with dimethyl methyl phosphonate (DMMP) and trimethyl phosphate (TMP), which are chemical warfare surrogates. The promoting effect of the agent and the species profiles were correctly reproduced. The decomposition reaction channels were studied; they included 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, as chemical warfare agents, in fire suppression [1–4], and in 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, L'Homme 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], triethyl-phosphonate (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 [14,15] 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 was 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

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TABLE 1
 Standard enthalpy of formation of selected compounds (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

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 was used to estimate the thermochemistry of a large number of phosphorus compounds. First six 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). Since 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 for the contribution of internal rotors that were not taken into account. The difference with BAC-MP4 calculations is less than 8 cal mol⁻¹, or 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 CH₃ or NH₂, -2 cal mol⁻¹ for C₂H₅, -2.5 cal mol⁻¹ for OCH₃, and +3.3 cal mol⁻¹ for H, F, or both.

Nineteen other group contributions were 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, and 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 an 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 PO₂ 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 700 K and 900 K. 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 3.10¹² and 10¹³ s⁻¹ [11,19]. We adopted the value of 10¹³ 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

TABLE 2
 Group contributions for organophosphorus compounds at 298 K

Group	ΔH_f^0 (kcal mol ⁻¹)	S^0 (cal K ⁻¹ mol ⁻¹)	C_p^0 (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

^aC-(H)₃(PO) \equiv C-(H)₃(CO) assigned for C_p^0 .

^bN-(H)₂(PO) \equiv N-(H)₂(CO) assigned.

^cS-(H)(PO) \equiv S-(H)(CO) assigned.

measured rate constants at 800 K. 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 assumed, 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 were 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 were 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 were 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 was 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 was exactly the initial one, but the start of the reaction was shifted by 10 ms.

Pre-exponential factors for the four-center eliminations were 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 PO₂ function, is then very low and should be below 2 kcal mol⁻¹.

TABLE 3
 Pyrolysis mechanism of DEMP, DIMP, and TEP

Reaction	$A \text{ (s}^{-1}\text{)}$	b	$E \text{ (cal mol}^{-1}\text{)}$
$\text{DEMP} \leftrightarrow \text{PO(OH)(OEt)(CH}_3\text{)} + \text{C}_2\text{H}_4$	1×10^{13}	0	45,300 ^a
$\text{PO(OH)(OEt)(CH}_3\text{)} \leftrightarrow \text{PO(OH)}_2\text{(CH}_3\text{)} + \text{C}_2\text{H}_4$	5×10^{12}	0	45,300
$\text{PO(OH)(OEt)(CH}_3\text{)} \leftrightarrow \text{CH}_3\text{PO}_2 + \text{C}_2\text{H}_5\text{OH}$	2.5×10^{13}	0	44,000
$\text{PO(OH)}_2\text{(CH}_3\text{)} \leftrightarrow \text{CH}_3\text{PO}_2 + \text{H}_2\text{O}$	5×10^{13}	0	39,000
$\text{DIMP} \leftrightarrow \text{PO(OH)(OiPr)(CH}_3\text{)} + \text{C}_3\text{H}_6$	2×10^{13}	0	41,200 ^a
$\text{PO(OH)(OiPr)(CH}_3\text{)} \leftrightarrow \text{PO(OH)}_2\text{(CH}_3\text{)} + \text{C}_3\text{H}_6$	1×10^{13}	0	41,200
$\text{PO(OH)(OiPr)(CH}_3\text{)} \leftrightarrow \text{CH}_3\text{PO}_2 + \text{C}_3\text{H}_7\text{OH}$	3.5×10^{13}	0	43,000
$\text{TEP} \leftrightarrow \text{PO(OH)(OEt)}_2 + \text{C}_2\text{H}_4$	2.8×10^{13}	0	45,300 ^a
$\text{PO(OH)(OEt)}_2 \leftrightarrow \text{PO(OH)}_2\text{(OEt)} + \text{C}_2\text{H}_4$	1.9×10^{13}	0	45,300
$\text{PO(OH)(OEt)}_2 \leftrightarrow \text{C}_2\text{H}_5\text{OPO}_2 + \text{C}_2\text{H}_5\text{OH}$	2.5×10^{13}	0	44,000
$\text{PO(OH)}_2\text{(OEt)} \leftrightarrow \text{PO(OH)}_3 + \text{C}_2\text{H}_4$	9.6×10^{12}	0	45,300
$\text{PO(OH)}_2\text{(OEt)} \leftrightarrow \text{HOPO}_2 + \text{C}_2\text{H}_5\text{OH}$	2.5×10^{13}	0	44,000
$\text{C}_2\text{H}_5\text{OPO}_2 \leftrightarrow \text{HOPO}_2 + \text{C}_2\text{H}_4$	1.9×10^{13}	0	45,300
$\text{PO(OH)}_2\text{(OEt)} \leftrightarrow \text{C}_2\text{H}_5\text{OPO}_2 + \text{H}_2\text{O}$	5×10^{13}	0	45,000
$\text{PO(OH)}_3 \leftrightarrow \text{HOPO}_2 + \text{H}_2\text{O}$	1.5×10^{14}	0	46,000

^aCalculated from Refs. [9–11], see text.

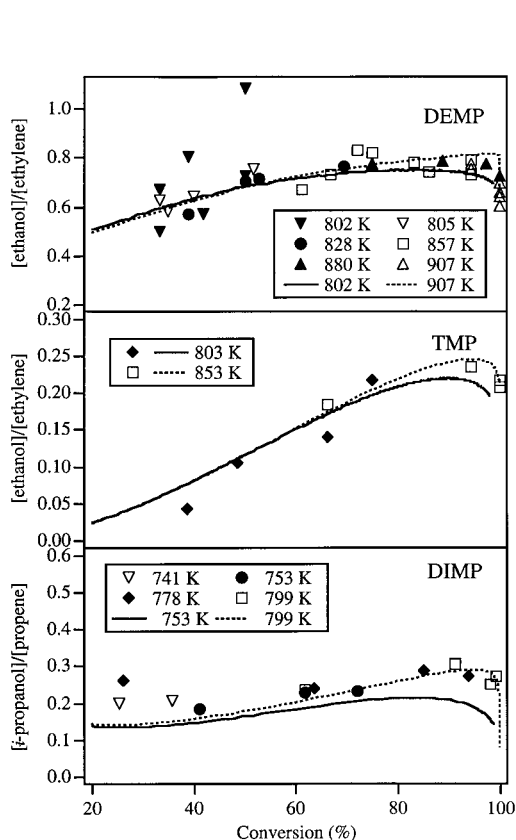


FIG. 1. Ratio of alcohol and alkene amount formed in the pyrolysis of DEMP [9], TEP [10], and DIMP [11] in flow reactor under 1 atm. Curves are model predictions.

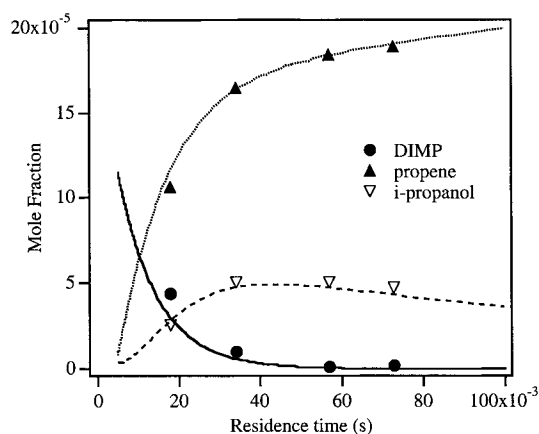
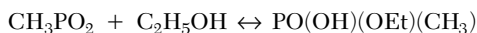


FIG. 2. Profiles of species in the pyrolysis of DIMP at 799 K in flow reactor under 1 atm [11]. Curves are model predictions.

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,



which produces the olefin,

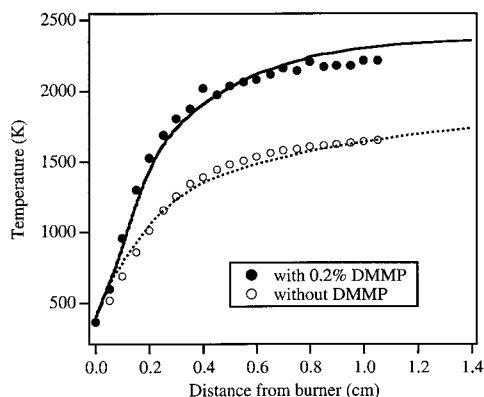


FIG. 3. Experimental and computed profiles of the temperature in the stoichiometric premixed $\text{H}_2/\text{O}_2/\text{Ar}$ flame [13] (mole fraction: 0.26/0.13/0.61), doped with 0.2% vol. of DMMP. $P = 80$ Torr.

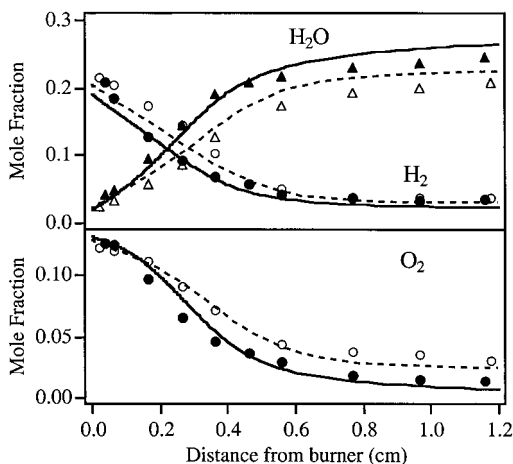


FIG. 4. Experimental and computed profiles of H_2 , O_2 , and H_2O in the stoichiometric premixed $\text{H}_2/\text{O}_2/\text{Ar}$ flame [15] (mole fraction: 0.26/0.13/0.61) with and without the addition of 0.2% vol. of TMP. $P = 47$ Torr. Curves are model predictions. Filled symbols and curves refer to the doped flame, open symbols and dashed curves refer to the undoped flame.

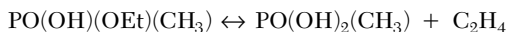


Fig. 2 shows reactants and carbonated products profiles for the pyrolysis of DIMP. The most important phosphorus product is then CH_3PO_2 , which is in equilibrium with water and *i*-propanol.

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 $\text{PO}(\text{OH})(\text{OCH}_3)_2$, $\text{PO}(\text{OH})(\text{CH}_3)(\text{OCH}_3)$, $\text{PO}(\text{OH})_2(\text{OCH}_3)$, $\text{PO}(\text{OH})_2(\text{CH}_3)$, $\text{PO}(\text{OH})_3$, 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 $\text{P}=\text{O}$ 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 $\text{P}=\text{O}$ were estimated, respectively, at $5.0 \times 10^{12} \exp(-5000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $1.4 \times 10^{12} \exp(-2000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by analogy with the addition to a $\text{C}=\text{O}$ bond.

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

This mechanism has been used to model the combustion of DMMP- and TMP-doped $\text{H}_2/\text{O}_2/\text{Ar}$ stabilized premixed stoichiometric flames in the experimental conditions of Korobeinichev [13,15]. The calculations were performed with the PREMIX [25] code. Fig. 3 compares computed and experimental temperature profiles of the flame with and without the addition of 0.2% DMMP [13]. The increased heat release when DMMP is added is well reproduced by the model. Fig. 4 compares the profiles of reactants and water obtained with and without the addition of TMP at the experimental conditions of Ref. [15]. 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 $\text{P}=\text{O}$ bond, followed by decomposition.

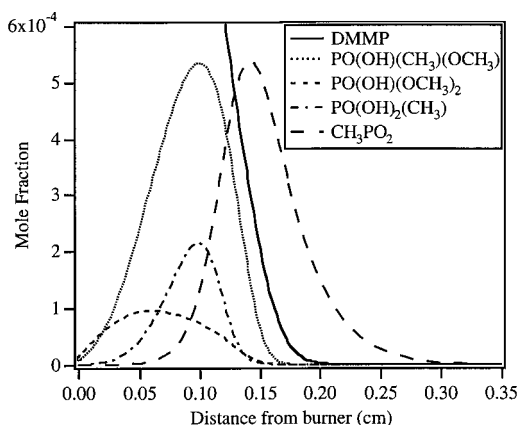


FIG. 5. Computed profiles of DMMP and intermediate phosphorus species in the stoichiometric premixed $\text{H}_2/\text{O}_2/\text{Ar}$ flame [13] (mole fraction: 0.26/0.13/0.61), doped with 0.2% vol. of DMMP, $P = 80$ Torr.

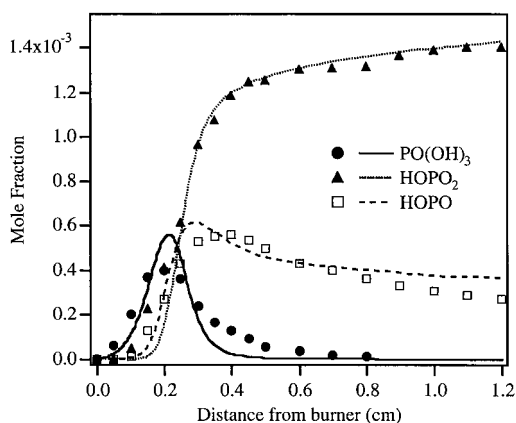


FIG. 6. Experimental and computed profiles of HOPO, HOPO₂, and orthophosphoric acid in the stoichiometric premixed $\text{H}_2/\text{O}_2/\text{Ar}$ flame [15] (mole fraction: 0.26/0.13/0.61) doped with 0.2% vol. of TMP. $P = 47$ Torr. Curves are model predictions.

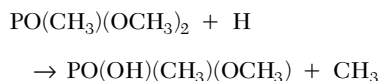


Fig. 5 shows computed profiles of DMMP and phosphorus intermediates at the experimental conditions of Ref. [13]. These compounds react mainly by H atom addition or a four-center elimination

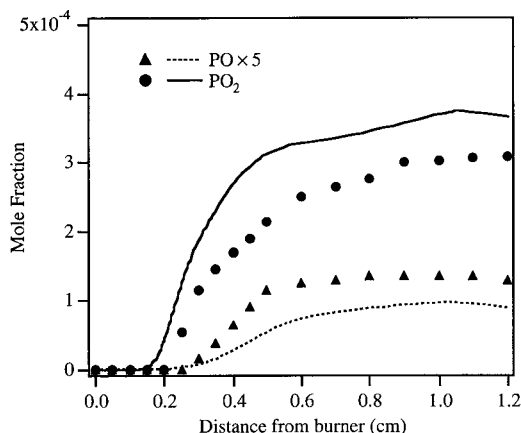
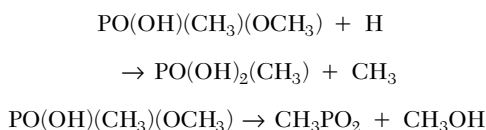
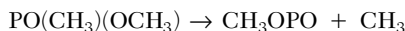
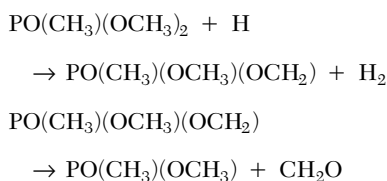


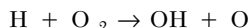
FIG. 7. Experimental and computed profiles of PO and PO₂ in the stoichiometric premixed $\text{H}_2/\text{O}_2/\text{Ar}$ flame [15] (mole fraction: 0.26/0.13/0.61) doped with 0.2% vol. of TMP. $P = 47$ Torr. Curves are model predictions.

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



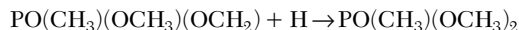
By addition of H radical, species as CH_3PO_2 or CH_3PO produce small oxides. These are orthophosphoric acid, HOPO, HOPO₂, and the radicals PO and PO₂. Figs. 6 and 7 compare experimental and calculated profiles of these species in the flame doped with TMP [15]. Near the burner, orthophosphoric acid is most stable, decomposing into HOPO₂ and water when the temperature increases. HOPO reacts mainly by H abstraction, giving PO₂, while H adds to HOPO₂ to give $\text{PO}(\text{OH})_2$ radical, which then combines with other radicals at lower temperatures or decomposes 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 the 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

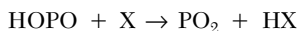
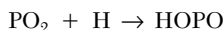


with a high activation energy of 16.5 kcal mol⁻¹.

The sensitivity analysis shows that in the very beginning of the H₂/O₂-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,



Later, the major termination effect comes from the cycle already proposed by Twarowski [18] that involves PO₂:



where X = H, O, or OH. Despite the loss of H atoms, which react otherwise with O₂ and produce chain branching, these termination cycles have a promoting effect because of the high exothermicity of H₂ or water formation. The present modeling results indicate that formation of the more stable HOPO₂, which reduces the termination cycles, has an inhibiting effect by reducing the amount of PO₂ radicals:



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



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 H₂/O₂ flames. This new mechanism, taking into account all possible intermediates, is more complete and comprehensive than previous ones. The model allows 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.

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COMMENTS

Richard G. Gann, NIST, USA. I am glad to see this mechanistic approach. Our work in the United States next generation fire suppression technology program indicates that chemically, phosphorus-containing compounds are effective in proportion to the number of P atoms added to the flame. This work is consistent with

the experimental finding. The exception may be the cyclic phosphonitriles, in which the phosphorus is very tightly bound. The Army Research Laboratory is looking into this at present.

Author's Reply. The comment requires no reply.