

Available online at www.sciencedirect.com



Combustion and Flame 140 (2005) 103-115

Combustion and Flame

www.elsevier.com/locate/jnlabr/cnf

# Flame inhibition by phosphorus-containing compounds over a range of equivalence ratios

T.M. Jayaweera<sup>a,1</sup>, C.F. Melius<sup>a</sup>, W.J. Pitz<sup>a,\*</sup>, C.K. Westbrook<sup>a</sup>, O.P. Korobeinichev<sup>b</sup>, V.M. Shvartsberg<sup>b</sup>, A.G. Shmakov<sup>b</sup>, I.V. Rybitskaya<sup>b</sup>, H.J. Curran<sup>c</sup>

<sup>a</sup> Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551-0808, USA
 <sup>b</sup> Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090 Russia
 <sup>c</sup> Department of Chemistry, National University of Ireland, Galway, Galway, Ireland

Received 17 May 2004; received in revised form 25 October 2004; accepted 2 November 2004

Available online 28 November 2004

## Abstract

There is much interest in the combustion mechanism of organophosphorus compounds (OPCs) due to their role as potential halon replacements in fire suppression. A continuing investigation of the inhibition activity of organophosphorus compounds under a range of equivalence ratios was performed experimentally and computationally, as measured by the burning velocity. Updates to a previous mechanism were made by the addition and modification of reactions in the mechanism for a more complete description of the inhibition reactions. Reaction pathways for  $HOPO_2 + H$  and HOPO + H are analyzed using the BAC-G2 approach. A new reaction pathway for HOPO<sub>2</sub> + H = PO<sub>2</sub> + H<sub>2</sub>O has been identified which results in a higher rate constant than that reported in the literature. In this work, the laminar flame speed is measured experimentally and calculated numerically for a premixed propane/air flame at 1 atm, under a range of equivalence ratios, undoped and doped with dimethyl methylphosphonate (DMMP). A detailed investigation of the catalytic cycles involved in the recombination of key flame radicals is made for two equivalence ratios, fuel lean and fuel rich. From this, the importance of different catalytic cycles involved in the lean versus rich case is discussed. The chemical kinetic model indicates that the  $HOPO_2 \Leftrightarrow PO_2$  inhibition cycle is more important in the lean flame than the rich. The OPCs are similarly effective across the range, demonstrating the robustness of OPCs as flame suppressants. In addition, it is shown that the phosphorus compounds are most active in the high-temperature region of the flame. This may, in part, explain their high level of inhibition effectiveness.

© 2004 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Flame inhibition; Organophosphorus compounds; Laminar flame speed; Detailed chemical kinetic modeling

# 1. Introduction

\* Corresponding author. Fax: +1-925-423-8772. *E-mail address:* pitz1@llnl.gov (W.J. Pitz).

<sup>1</sup> Current address: FM Global, Norwood, MA 02062.

For many years, halogenated hydrocarbons, such as  $CF_3Br$ , were used as fire suppressants. However, due to their high ozone depletion potential, they are no longer being manufactured in industrialized coun-

0010-2180/\$ – see front matter © 2004 The Combustion Institute. Published by Elsevier Inc. All rights reserved. doi:10.1016/j.combustflame.2004.11.001

tries, as stipulated in the 1990 Montreal Protocol. The search for effective replacements has led to a family of organophosphorus compounds (OPCs) that have shown considerable promise as flame inhibitors [1–3]. Early work of Twarowski [4–6] demonstrated that phosphine (PH<sub>3</sub>) accelerated radical recombination in hydrogen oxidation, and subsequent work by Korobeinichev et al. began to explain how OPCs inhibited hydrogen flames [7] and hydrocarbon flames [8].

Chemically active flame inhibitors alter flame chemistry by catalytic recombination of key flame radicals, especially H and O atoms and OH radicals. H atoms are particularly important in flame propagation, since the principal chain branching reaction in hydrogen and hydrocarbon flames is H +  $O_2 \rightarrow OH + O$ . Fast elementary reactions interconnect these small radical species, and removal of any of them through recombination reduces concentrations of all of them correspondingly. Therefore, radical recombination leads to fewer H atoms in the reaction zone, which leads to reduced chain branching and a lower burning velocity in a premixed flame. This applies to familiar halogenated suppressants such as HBr and CF<sub>3</sub>Br [9,10] and OPCs such as dimethyl methylphosphonate (DMMP) [11].

In his studies on addition of small amounts of phosphine combustion products to water vapor, Twa-rowski [4–6] found that small P-containing species promote catalytic recombination of radicals:

$$PO_2 + H + M \rightarrow HOPO + M,$$
 (1a)

 $HOPO + H \to H_2 + PO_2, \tag{1b}$ 

 $PO_2 + OH (+M) \rightarrow HOPO_2 (+M),$  (2a)

$$HOPO_2 + H \to H_2O + PO_2. \tag{2b}$$

These reaction sequences act as termination reactions, converting highly reactive H and OH radicals to molecular species  $H_2$  or  $H_2O$ , the latter being a stable combustion product. In the present work, we will be focusing on these catalytic recombination reactions.

This work extends a previous investigation of phosphorus-doped premixed flames, by the same authors [12]. In the previous work, phosphorus-doped premixed flames were investigated with respect to their species concentrations profiles under a lean and rich condition in a flat flame burner (equivalence ratios of 0.9 and 1.2). In the present work, flame speeds are investigated over a range of equivalence ratios in a Mache–Hebra nozzle burner [13,14]. We also examine the effect of equivalence ratio on the key inhibition cycles.

# 2. Experimental work

The speed of premixed  $C_3H_8/air$  flames was measured using a Mache–Hebra nozzle burner [13,14] at 1 atm and the total area method using an image of the flame. The experimental technique is described in detail elsewhere [8]. To evaluate the influence of a heat loss from the flame to the burner on the measured values, the speed of undoped propane/air flames of various stoichiometries was measured for an unburned gas temperature of 298 K. The obtained result of 41.7 cm/s for a stoichiometric flame is comparable with experimental data measured by different techniques [15–17]. This comparison gives validity to the method used for the measurement of flame burning velocities.

In addition, we measured the flame speed of DMMP-doped propane/air flames at 1 atm and over a range of equivalence ratios. The fuel/air equivalence ratio was varied from 0.8 to 1.3 in 0.1 increments. In this case, to minimize condensation of DMMP on the burner surface, the reactant temperature was increased to 368 K. The loadings tested were 0, 300, and 600 ppm of DMMP. The results from these experiments are shown in Fig. 1. Uncertainty in measured values is included in the figure for the undoped flame. The same percentage error can be applied for the doped flames. The main source of uncertainty in measuring burning velocity is from the measurement of the contour of the flame cone. The flame cone is blurred and the maximum blurring occurs for the fuelrich case. Additionally, the uncertainty in the dopant loading is  $\pm 40$  ppm and the relative uncertainty in the equivalence ratio is  $\pm 2\%$ .



Fig. 1. Experimentally measured flame speed, over a range of equivalence ratios, for propane/air flames with various loadings of DMMP (0, 300, and 600 ppm) and for an unburned reactant temperature of 368 K. Error bars are shown on undoped data, but the same percentage uncertainty can be applied to the doped data, as well.



Fig. 2. Potential energy surface for the conversion of  $HOPO_2 + H$  to products. Numbers given are the enthalpies (kcal/mol) for the compounds as well as the various transition states.

## 3. Modeling approach

### 3.1. Phosphorus mechanism

The chemical kinetic mechanism is based on a mechanism previously described by Korobeinichev et al. [12]. As described there, this mechanism has important updates in the species thermochemistry and in the reaction mechanism. The thermochemistry for the key phosphorus species,  $PO_xH_y$ , was recalculated using a more accurate method (BAC-G2). In addition, a more complete analysis of the reaction pathways was performed.

A new reaction pathway by which HOPO<sub>2</sub> can be converted to PO<sub>2</sub> and H<sub>2</sub>O, augmenting the direct reaction (2b) above, was developed. Although the basics of these reactions are described in another paper [12], further details are given here. Reaction (2b) is treated as a multichannel reaction:

$$\begin{split} & \text{HOPO}_2 + \text{H} \leftrightarrow \text{HPO}(\text{OH})\text{O} \leftrightarrow \text{PO}(\text{OH})_2 \\ & \rightarrow \text{H}_2\text{O} + \text{PO}_2, \end{split} \tag{2c}$$

$$HOPO_2 + H \leftrightarrow PO(OH)_2 \rightarrow H_2O + PO_2.$$
 (2d)

The potential energy surface (PES) for this set of reactions is given as Fig. 2. It is very similar to that obtained by Mackie [18] but includes the additional pathway via HPO(OH)O, reaction (2). The addition of a hydrogen atom to the phosphorus atom (reaction (2c)) has no barrier and the 1, 2 hydrogen shift to PO(OH)<sub>2</sub> is only 1.5 kcal/mol above the incoming reactants. Consequently, reaction (2c) is almost 10 times faster at 1500 K than reaction (2d) which has a barrier of 8 kcal/mol. Since the contribution of reaction (2d) is small, it was omitted from the reaction mechanism.

The pressure dependence of the HOPO<sub>2</sub> + H system was recomputed using the BAC-G2 barrier heights. Rate constants for the reaction paths in Fig. 2

were estimated using Quantum RRK analysis to obtain k(E) and master equation analysis [19] to evaluate pressure fall off. For the master equation analysis, an exponential-down energy-transfer model was used, with a collisional step-size down ( $\Delta E_{\text{down}}$ ) = 142.9(T/300)<sup>1.297</sup> cm<sup>-1</sup>. These values were based on the step-size down used by Tsang and Herron for the  $NO_2 + OH$  system [20]. The bath gas was air and Lennard-Jones parameters for the adduct are a cross section of 5.5 Å and  $\varepsilon/k$  of 250 K. Our analysis shows more stabilization to form the PO(OH)2 adduct than reported by Mackie et al. [18]. At 1000 K, our rate constant of  $HOPO_2 + H = PO_2 + H_2O$  drops by 65% due to stabilization when the pressure is increased from 1 to 10 atm, whereas the Mackie et al. rate constant decreases by 39% (Table 5 in [18]). We attribute this difference to our use of a much larger collisional step-size down. At 1300 K where the HOPO<sub>2</sub> + H reaction is particularly important in the DMMP-doped flame, 25% of the reaction throughput goes to stabilization (PO(OH)<sub>2</sub>) according to our calculations. The reaction throughput to PO(OH)2 increases to 86% at 100 atm. We have included rate constant expressions at various pressures in our Chemkin formatted mechanism discussed later.

A similar BAC-G2 analysis was also done for HOPO + H, reaction (1b) given above, which is treated as a multichannel reaction:

$$HOPO + H \to PO_2 + H_2, \tag{1c}$$

$$\begin{split} \text{HOPO} &+ \text{H} \leftrightarrow \text{PH(OH)O} \leftrightarrow \text{P(OH)}_2 \\ &\rightarrow \text{PO} + \text{H}_2\text{O}, \end{split} \tag{1d}$$

$$HOPO + H \leftrightarrow P(OH)_2 \rightarrow PO + H_2O.$$
(1e)

The potential energy surface for this reaction is given in Fig. 3. Because of a high preexponential factor, the abstraction path (1c) dominates and paths (1d) and (1e) play a minor role. In this case, the addition of an H atom to the phosphorus atom (1d) did



Fig. 3. Potential energy surface for HOPO + H to products. Numbers given are the enthalpies (kcal/mol) for the compounds as well as the various transition states.

not give an overall barrier to products lower than the addition to the oxygen atom (path (1e)) as was seen in the HOPO<sub>2</sub> + H reaction pathway. Also included on both these PESs are other reactions that go through the same intermediary species. These reactions are HOPO + OH and HPO<sub>2</sub> + OH in Fig. 2 and HPO + OH in Fig. 3. As one can see in this figure, the phosphorus can start in a variety of forms (HOPO, HOPO<sub>2</sub>, HPO, or HPO<sub>2</sub>), but will eventually end with PO<sub>2</sub> + H<sub>2</sub>O as products. This demonstrates how PO<sub>2</sub> is a central species in the inhibition cycles, regardless of the oxidation level of the PO<sub>x</sub>H<sub>y</sub> species present.

Further modifications were made to try and improve estimates of various reaction rates. The preexponential factors (A) of the PO + OH, O, H and  $PO_2 + O$  recombination reactions (reactions (27), (36), (41), and (56) in Table 1) were reduced from the values used in Ref. [12] to match the values reported in Twarowski [6]. (Note that Twarowski's rate constant expressions must be refit to Arrhenius form to use them in Chemkin [21].) The A factors of reactions (27), (36), (41), and (56) had been increased in Ref. [21] by factors of 10, 5, 10, and 5, respectively, to get good agreement with measured species profiles in hydrogen/organophosphorus flames [27]. With the improvements in the mechanism, the authors thought that these multiplicative factors should be removed so that Twarowski's original rate constant estimates could be used. His estimates were based on estimated high-pressure limits for radical-radical and radical-atom reactions and RRKM analysis [6]. This change in the mechanism degraded the agreement between the computed and the measured species profiles for the lean case in the burner-stabilized flames reported in Ref. [12]. The new comparison between the computed and the measured profiles for the burnerstabilized flames is given in the supplemental material. Part of the reaction mechanism is given in Table 1 for the small phosphorus-containing species. The complete organophosphorus hydrocarbon mechanism in Chemkin format including the thermodynamic and transport data for the species is available as supplemental material, electronically from our website [24] and from the corresponding author.

## 3.2. Computational model

In this work, PREMIX, in the Chemkin 3.7.1 suite of programs [21], was used to calculate the laminar burning velocity. A freely propagating premixed flame of C3H8/air, with and without dimethyl methylphosphonate, was studied. The equivalence ratio ( $\phi$ ) was varied from 0.8 to 1.3 in 0.1 increments and the DMMP loadings tested were 0 and 600 ppm, to match the experimental work. For reference, Figs. 4a and 4b give the major species and temperature profiles for the doped lean ( $\phi = 0.8$ ) and rich  $(\phi = 1.3)$  flames, respectively. The reactants were at atmospheric pressure with an initial temperature of 368 K, again to match the experimental conditions. In all calculations, the energy equation was solved, and mixture-averaged diffusion was used. Windward differencing was used and the grid was refined down to a value of GRAD = 0.1 CURV < 0.2 (parameters that control the number of grid points inserted in regions of high gradient and high curvature in PREMIX [21]). These values of GRAD and CURV supplied a sufficient refinement of the grid such that the flame speed was independent of number of grid points (~200-250 required).

A recently refined high-temperature propane oxidation mechanism [22] with updated thermodynam-

Table 1 Reaction mechanism for small phosphorus-containing species

No.	Reaction	Α	п	Ea	Reference
1.	$PO_2 + PO(+m) = P_2O_3(+m)$	4.00e+14	-1.00	0.00	а
	Low-pressure limit:	1.00e + 20	-2.00	0.00	
2.	$PO_2 + PO_2 (+m) = P_2O_4 (+m)$	6.00e+14	-1.00	0.00	а
	Low-pressure limit:	2.00e + 20	-2.00	0.00	
3.	$PO_2 + PO_3 (+m) = P_2O_5 (+m)$	6.00e+14	-1.00	0.00	а
	Low-pressure limit:	5.00e + 20	-2.00	0.00	
4.	$PO_2 + OH + m = HOPO_2 + m$	1.60e + 24	-2.28	2.85e+02	0
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				h
5.	$PO_3 + H + m = HOPO_2 + m$	4.80e + 24	-2.37	1.43e+03	U
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				h
6.	$HOPO + O + m = HOPO_2 + m$	1.20e + 27	-2.99	2.04e + 03	b
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				~ £
7.	$H_2 + PO_3 = HOPO_2 + H$	2.00e+12	0.00	0.00	C,I
8.	$HOPO + OH = PO_2 + H_2O$	3.72e+13	-0.22	3.20e+03	[18] <sup>d</sup>
9.	$HOPO_2 + H = PO(OH)_2$	1.27e+32	-6.10	8.70e+03	e
10.	$HOPO_2 + H = PO_2 + H_2O$	5.16e+19	-1.83	1.07e + 04	e
11.	$PO(OH)_2 = PO_2 + H_2O$	1.45e + 28	-4.97	4.46e + 04	e
12.	$HOPO_2 + OH = PO(OH)_2O$	1.00e+19	-2.00	0.00	a
13.	$PO(OH)_2O + H = HOPO_2 + H_2O$	2.00e+13	0.00	0.00	a
14.	$PO(OH)_2 + H = HPO_2 + H_2O$	4.00e+19	-2.00	0.00	t
15.	$PO(OH)_2 + OH = HOPO_2 + H_2O$	2.00e+13	0.00	0.00	а
16.	$PO(OH)_2 + H = HOPO_2 + H_2$	5.00e+12	0.00	0.00	a
17.	$PO(OH)_2 + OH = PO(OH)_3$	1.00e+13	0.00	0.00	f
18.	$PO(OH)_2 + O = HOPO_2 + OH$	5.00e+13	0.00	0.00	f
19.	$P_2O_4 + H_2O = HOPO + HOPO_2$	1.00e+11	0.00	0.00	а
20.	$P_2O_5 + H_2O = HOPO_2 + HOPO_2$	1.00e+11	0.00	0.00	a
21.	$HOPO_2 + O = OH + PO_3$	1.00e+13	0.00	1.23e + 04	f,s
22.	$HOPO_2 + OH = H_2O + PO_3$	1.20e + 06	2.00	2.00e+03	f,t
23.	$HO_2 + HOPO = HOPO_2 + OH$	1.50e + 14	0.00	2.36e + 04	g,f
24.	$HOPO_2 + HO_2 = H_2O_2 + PO_3$	2.50e+12	0.00	2.46e + 04	h,f
25.	$HOPO_2 + O_2 = HO_2 + PO_3$	7.00e+12	0.00	6.60e + 04	j,f
26.	$HOPO_2 + CH_3 = CH_4 + PO_3$	1.50e+12	0.00	1.31e+04	k,f
27.	PO + OH + M = HOPO + M	1.00e+21	-2.09	1.59e + 03	b
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
28.	$PO_2 + H + M = HOPO + M$	4.87e+24	-2.04	6.45e+02	b,d,p
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
29.	$HOPO + H = H_2 + PO_2$	1.00e+13	0.00	1.10e+04	а
30.	$HOPO + O = OH + PO_2$	1.00e+13	0.00	0.00	f
31.	$HOPO + O = H + PO_3$	1.00e+12	0.00	1.50e + 04	f
32.	$HOPO + OH = PO_2 + H_2O$	1.20e+06	2.00	-1.50e+03	1,d
33.	$HOPO + HO_2 = H_2O_2 + PO_2$	2.50e+12	0.00	2.33e+04	f
34.	$HOPO + O_2 = HO_2 + PO_2$	7.00e+12	0.00	4.53e+04	j
35.	$HOPO + CH_3 = CH_4 + PO_2$	1.50e+12	0.00	1.31e+04	f
36.	$PO + O + M = PO_2 + M$	1.60e + 25	-2.63	1.72e+03	b
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
37.	$PO + OH = H + PO_2$	1.00e+13	0.00	0.00	n
38.	$PO + HO_2 = PO_2 + OH$	2.10e+12	0.00	-5.00e+02	q,f
	=				

(continued on next page)

Table 1 (continued)

No.	Reaction	Α	п	Ea	Reference
39.	$PO + O_2 = PO_2 + O$	1.00e+12	0.00	0.00	r
40.	$PO + CH_3 = CH_3PO$	1.00e+13	0.00	0.00	f
41.	$PO_2 + O + M = PO_3 + M$	1.30e + 27	-3.15	1.88e+03	b
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
42.	$H + PO_3 = PO_2 + OH$	3.16e+13	0.00	4.00e+01	[6]
43.	$PO_2 + HO_2 = OH + PO_3$	5.00e+11	0.00	0.00	f
44.	$PO_2 + O_2 = O + PO_3$	1.00e+12	0.00	3.00e+04	f
45.	$CH_3 + PO_2 = CH_3PO_2$	6.30e+14	-0.60	0.00	f,u
46.	$CH_3 + PO_2 = CH_3OPO$	2.10e+12	-0.60	0.00	f,w
47.	$PO_2 + CH_3 = CH_3O + PO$	5.00e+11	0.00	4.33e+04	f
48.	$PO_2 + CH_3O = CH_2O + HOPO$	1.00e+13	0.00	0.00	f
49.	$HOPO + PO_3 = PO_2 + HOPO_2$	5.00e+11	0.00	0.00	f
49.	$PO_3 + PO = PO_2 + PO_2$	5.00e+11	0.00	0.00	f
50.	$CH_3 + PO_3 = CH_3OPO_2$	5.00e+11	0.00	0.00	f
51.	$PO_3 + CH_3 = CH_3O + PO_2$	5.00e+11	0.00	1.53e + 04	f
	Rev	5.00e+11	0.00	1.10e + 04	
52.	$PO_3 + CH_3O = CH_2O + HOPO_2$	1.00e+13	0.00	0.00	f
53.	$CH_3PO + H = CH_3 + HPO$	1.00e+13	0.00	6.00e+03	f
54.	$CH_3PO + O = CH_3 + PO_2$	1.00e+13	0.00	0.00	f
55.	$CH_3PO_2 = CH_3PO + O$	1.00e + 14	0.00	1.33e+05	f
56.	H + PO + m = HPO + m	1.80e + 22	-1.95	1.33e+3	0
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
57.	$HPO + H = H_2 + PO$	2.40e + 08	1.50	0.00	f
58.	HPO + O = OH + PO	1.70e + 08	1.50	0.00	f
59.	$HPO + O = PO_2 + H$	1.00e+13	0.00	3.00e+03	f
60.	$HPO + O_2 = PO + HO_2$	7.00e+12	0.00	2.00e+04	f
61.	$HPO + OH = PO + H_2O$	1.20e + 06	2.00	-2.00e+03	f
62.	HPO + OH = PO(H)(OH)	1.40e+12	0.00	0.00	f
63.	$HOPO + H = H_2O + PO$	3.00e+12	0.00	8.30e+03	х
64.	$PO(H)(OH) + H = HOPO + H_2$	5.00e+13	0.00	0.00	f
65.	$PO(H)(OH) + OH = HOPO + H_2O$	1.00e+13	0.00	0.00	f
66.	PO(H)(OH) + O = HOPO + OH	5.00e+13	0.00	0.00	f
67.	$HPO + HO_2 = PO + H_2O_2$	2.00e+11	0.00	5.00e+03	f
68.	$HPO + PO_2 = PO + HOPO$	2.00e+11	0.00	0.00	f
69.	$HPO + PO_3 = PO + HOPO_2$	2.00e+11	0.00	0.00	f
70.	$HPO + CH_3 = PO + CH_4$	8.10e+05	1.87	0.00	f
71.	$H + PO_2 + m = HPO_2 + m$	4.87e+21	-2.04	6.45e+02	У
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
72.	$H + PO_2 + m = HOPO + m$	4.87e+23	-2.04	6.45e+02	z,d
	Enhanced third-body efficiencies:				
	$H_2O = 16, H_2 = 2.5$				
73.	$HPO_2 = HOPO$	2.35e+14	0.00	4.64e + 04	aa
74.	$HPO_2 + H = H_2 + PO_2$	2.40e + 08	1.50	5.00e+03	f
75.	$HPO_2 + H = PO(H)(OH)$	5.00e+12	0.00	5.00e+03	f
76.	$HPO_2 + O = OH + PO_2$	1.70e + 08	1.50	2.50e+03	f
77.	$HPO_2 + O_2 = PO_2 + HO_2$	7.00e+12	0.00	3.44e + 04	t
78.	$HPO_2 + OH = H_2O + PO_2$	1.20e + 06	2.00	-2.00e+03	f
79.	$HPO_2 + OH = H + HOPO_2$	1.00e+12	0.00	2.00e+03	f
80.	$HPO_2 + HO_2 = H_2O_2 + PO_2$	2.00e+11	0.00	1.00e+04	f
81.	$HPO_2 + CH_3 = CH_4 + PO_2$	8.10e+05	1.87	7.00e+03	f
82.	$HPO + PO_2 = HPO_2 + PO$	1.00e+11	0.00	0.00	f

(continued on next page)

Table 1 (continued)

No.	Reaction	Α	п	$E_{a}$	Reference
83.	$HPO_2 + PO_2 = HOPO + PO_2$	5.00e+11	0.00	0.00	f
84.	$HPO_2 + PO_3 = HOPO_2 + PO_2$	5.00e+11	0.00	0.00	f

Rate constant fit to the form  $AT^n \exp(-E_a/RT)$ . Units: cal, cm<sup>3</sup>, mol, s. Enhanced third-body efficiencies are relative to N<sub>2</sub>. For reactions of the form, a + b + m = ab + m the rate constant is the low-pressure limit expression. For reaction of the form a + b (+m) = c (+m), the rate constant in the first line is the high-pressure limit.

<sup>a</sup> Estimate.

<sup>b</sup> Rate from [6]. Rate expression refit to Arrhenius form.

<sup>c</sup> Forward A factor is computed from reverse A factor and microscopic reversibility. Reverse A factor is from  $CH_3OH + H = CH_3O + H_2$ . Forward  $E_a$  estimated to be zero for H abstraction.

<sup>d</sup> Duplicate reaction: The mechanism has more than one reaction with identical reactants and products but the reaction represents different reaction channels. (For example, abstraction and addition channels.)

<sup>e</sup> Chemaster value. Rate constant fit at 1 atm, 300–2400 K, see text.

<sup>f</sup> Glaude estimate from [27].

<sup>g</sup> Analogy with  $CO + HO_2 = CO_2 + OH$  [28].

<sup>h</sup> Analogy with  $C_2H_5OH + HO_2 = C_2H_5O + H_2O_2$  [29].

<sup>j</sup> Based on Walker recommendation for  $RH + O_2 = R + HO_2$  [30].

<sup>k</sup> Analogy with  $CH_3OH + CH_3 = CH_3O + CH_4$  [31].

<sup>1</sup> Abstraction route. Used reaction rate rule for ROH + OH = RO + H<sub>2</sub>O from [32]. Used  $E_a$  for tertiary H–C to match H–O bond strength in HOPO.

<sup>n</sup> Estimate based on radical-radical recombination rate.

- <sup>o</sup> Rate from [6]. Rate expression refit to Arrhenius form by Werner and Cool [33].
- <sup>p</sup> Addition of H to O on PO<sub>2</sub>. Twarowski's rate constant increased by a factor of 3 by Wainner et al. [34].
- <sup>q</sup> Based on NO +  $HO_2 = NO_2 + OH$  from [35].

<sup>r</sup> Estimated based on tight transition state with no barrier.

<sup>s</sup> Forward A factor is from CH<sub>3</sub>OH + O = CH<sub>3</sub>O + OH [36]. Forward  $E_a$  computed from reverse  $E_a$  and microscopic reversibility. Reverse  $E_a$  is zero from Evans–Polanyi plot [37].

<sup>t</sup> Estimated to be the same rate constant as  $H_2O + OH = H_2O + OH$ .

- <sup>u</sup> Analogy with  $CH_3 + NO_2 \Rightarrow CH_3NO_2$  [38].
- <sup>w</sup> Analogy with  $CH_3 + NO_2 \Rightarrow CH_3ONO$  [39].

<sup>x</sup> Addition path from Mackie et al.'s value [40]. Decreased A factor.

<sup>y</sup> H adding to P of PO<sub>2</sub>. Assume 1% of the incoming channel is stabilized as HPO<sub>2</sub> adduct.

 $^{z}$  H adding to P of PO<sub>2</sub>. Assume almost all of the incoming channels goes through chemically activated route to HOPO. Rate constant from Wainner et al. [34].

<sup>aa</sup> Rate constant computed from BACMP4. The cis form of the TST was used [41-43].

ics parameters was used for the hydrocarbon species in the chemical kinetic mechanism. At T = 300 K, P = 1 atm and  $\phi = 1$ , this mechanism computes a laminar burning velocity of 41.1 cm/s, in good agreement with our own experimental value above and other experimental studies (e.g., 39 cm/s [23]). Further validation has been performed comparing computed results with the propane mechanism with measured results from shock-tube, flow reactor, stirred reactor, and premixed laminar flame studies [22].

#### 4. Results and discussion

The new mechanism was used to calculate the effect of 600 ppm of DMMP on a propane/air flame with varying equivalence ratios. Two measures can be used to measure the effectiveness of an inhibitor on a premixed flame: change in radical concentration and change in laminar burning velocity. Both shall be discussed here, focusing on the  $\phi = 0.8$  and  $\phi = 1.3$  flames.

As described above, a dopant acts to inhibit a flame by radically recombining the key flame radicals, namely H and OH. Thus, a plot of the concentrations of these two species across a flame with and without a dopant is a useful tool. Given in Figs. 5a and 5b are the mole fractions of H and OH with and without 600 ppm of DMMP for the lean and rich flames, respectively. The solid lines represent the undoped flame, while the dashed lines include the effect of DMMP. As is apparent in these figures, the DMMP is reducing the concentration of the flame radicals fairly significantly in the two flames. It appears that in the rich flame, there is a greater reduction of H, than in the lean flame. This effect will be explored further below.

Fig. 6 gives the calculated flame speeds for the undoped and 600 ppm DMMP-doped flames. The curve represents a second-order polynomial fit of the data. As can be seen, the data fall well onto the line, al-



Fig. 4. (a) Major species and temperature profiles in the lean ( $\phi = 0.8$ ), doped flame. (b) Major species and temperature profiles in the rich ( $\phi = 1.3$ ), doped flame. A distance of zero is at the cold boundary of the flame.

though there is a small amount of numerical scatter. It appears that there is little difference in the effectiveness of the lean and rich flame. To further explore this, the difference in flame speeds between the undoped and doped flames as a function of equivalence ratio was plotted in Fig. 7 on a normalized basis:  $(Su_0 - Su)/Su_0$ . The flame speeds were normalized to compare the fractional reduction in flame speed as a function of equivalence ratio from the experiments and model. Two points can be made from this figure. First, the mechanism does a reasonable job at predicting the measured inhibition effectiveness of the DMMP across the range of equivalence ratios. It should be noted that, as can be observed in Fig. 1, the uncertainty in the experimental measurements are relatively large in the rich flame, thus making it difficult to make a precise comparison between the experimental and the computational results.

Secondly, according to the calculations, the DMMP appears to be monotonically increasing in effectiveness with equivalence ratio. This effect also appeared



Fig. 5. (a) Comparison of OH and H profiles in the undoped (solid line) and doped (dashed line) lean flame. (b) Comparison of OH and H profiles in the undoped (solid line) and doped (dashed line) rich flame.



Fig. 6. Flame speed, as a function of equivalence ratio, for the undoped and doped flames calculated using PREMIX. The curves represent a fitted, second-degree polynomial.



Fig. 7. Normalized flame speed for the experimentally measured and numerically calculated propane/air flames doped with 600 ppm of DMMP over a range of equivalence ratios. The line is a linear fit of the numerical data.

in comparing Figs. 5a and 5b where the rich flame decreased the H concentration more than the lean flame. However, this effect is not apparent in the experimental work, and so it may imply that the mechanism needs more refinement. There is still some future work that can be performed, particularly in the rich flame condition. Most of the emphasis thus far in mechanism refinement has been focused on the activity of the H and OH radicals with the phosphorus oxy-acids. However in a rich flame condition, the interaction of phosphorus compounds with  $CH_3$  and other hydrocarbon species could play a large role and further investigation into their reactions should be performed.

Nonetheless, there is no difference in the observed effectiveness of DMMP in the rich and lean flames in the experiments and only a moderate difference in the calculations. One might actually expect a larger difference in effectiveness in the two flames, as the radical species present in a lean, or highly oxidized flame, are different than in a rich flame. To understand how the phosphorus compounds perform under different equivalence ratios, a detailed investigation of the inhibition cycles of two equivalence ratios ( $\phi = 0.8$  and 1.3) was performed.

To do this, an evaluation of key phosphorus species involved in the recombination of H and OH was evaluated using PREMIX [21]. Fig. 8a plots the profiles of the key phosphorus-containing reactions involved in the production/destruction of PO<sub>2</sub> (using rate of production, ROP in mol/cm<sup>3</sup>/s, values from the postprocessor of PREMIX) across the lean ( $\phi = 0.8$ ) flame. The same plot for the rich flame ( $\phi = 1.3$ ) is given in Fig. 8b. For clarity, only the top few reactions are included. As can be seen in the figure for both flames, the primary reaction for PO<sub>2</sub>



Fig. 8. (a) Rate of production of  $PO_2$  due to various reactions in the lean flame. (b) Rate of production of  $PO_2$  due to various reactions in the rich flame.

production is HOPO + OH  $\rightarrow$  PO<sub>2</sub> + H<sub>2</sub>O. This is expected for lean flames, which usually have high OH levels. For the rich flame, one might expect that HOPO + H  $\rightarrow$  PO<sub>2</sub> + H<sub>2</sub> plays a significant role because H-atom concentrations are usually higher and OH concentrations lower in rich compared to lean flames. However, this reaction is not significant due to the higher activation energy of the reaction of HOPO with H (11 kcal/mol) compared with OH (-1.5 kcal/mol).

The same key reaction for PO<sub>2</sub> consumption for both flames is PO<sub>2</sub> + H + M  $\rightarrow$  HOPO + M. Together, it forms a catalytic cycle with HOPO + OH  $\rightarrow$  PO<sub>2</sub> + H<sub>2</sub>O where the net effect is that H and OH recombine to form H<sub>2</sub>O. Although this reaction cycle is the most important one for both lean and rich cases, a more detailed evaluation of the key reaction cycles in flame suppression can be made, as well as an estimate of the location in the flame at which they occur.



Fig. 9. (a) Sensitivity of H concentration due to phosphorus species in lean flame. (b) Sensitivity of H concentration due to phosphorus species in rich flame.

A sensitivity analysis was performed to determine which reactions are most important in affecting the H-atom concentration, a key indicator of inhibition in the flame. The analysis was performed using the PREMIX code which computes first-order sensitivity coefficients. In this case, they are defined as the normalized derivative of the H atom mass fraction with respect to the A factor of an individual reaction. A negative sensitivity indicates that increasing the reaction rate decreases the H-atom concentration, thus inhibiting the flame, and a positive sensitivity indicates the opposite. Figs. 9a and 9b plot these results, for the lean and rich flame, respectively, only including the effect of reactions involving  $PO_xH_y$ species. Note, the key radical propagation reaction,  $H + O_2 \rightarrow OH + O$ , is not included in these figures as its magnitude would overwhelm the other reactions. Results for OH are similar, so they are not plotted.

The maximum sensitivity to the various phosphorus reactions occurs in the primary reaction zone of the flame. However, the phosphorus reactions have their primary activity in the postflame region, as seen in the rate-of-production plots. As is apparent in these figures, the chief phosphorus reaction to which the H atom is sensitive is  $PO_2 + H \rightarrow HOPO$ . This is also seen in the rate-of-production plots given above. The H-atom concentration is also very sensitive to the  $HOPO_2 + H \rightarrow PO_2 + H_2O$  reaction in the lean flame. The rate constant of this reaction was increased due to inclusion of the new reaction path (2c) discussed earlier.

One curious aspect to note is that the H atom has a positive sensitivity to  $PO_2 + OH \rightarrow HOPO_2$  in the lean flame (Fig. 9a). This result indicates that increasing its reaction rate promotes H-atom production in the flame. In the rich flame, the sensitivity of this reaction is not significant. One would think that H and OH would be negatively sensitive to any reaction involved in H/OH recombination, but this reaction has the opposite effect. We believe that the change in sign is due to the HOPO  $\Leftrightarrow$  PO<sub>2</sub> cycle being the most efficient in recombining H and OH radicals. By introducing HOPO<sub>2</sub>, the phosphorus is effectively being taken away from the HOPO cycle and thus, less H and OH are being recombined. This suggests that HOPO is a better catalyst for recombination than HOPO<sub>2</sub>. In the lean flame, where HOPO<sub>2</sub> is more prevalent than in the rich flame (as will be discussed below), one might expect phosphorus to be less effective in the lean flame. In Fig. 7, the numerical results indicate that the phosphorus is less effective in reducing the flame speed under lean conditions.

The results for the remaining reactions in the sensitivity analysis can best be understood in terms of the HOPO  $\Leftrightarrow$  PO<sub>2</sub> cycle being more efficient than the HOPO<sub>2</sub>  $\Leftrightarrow$  PO<sub>2</sub> cycle. Increasing the rate constants of reactions that send reactive flux to the more efficient HOPO  $\Leftrightarrow$  PO<sub>2</sub> cycle causes more H and OH radical recombination, gives negative sensitivities, and inhibits the flame. Increasing the rate constants of reactions that send more flux to the less efficient HOPO<sub>2</sub>  $\Leftrightarrow$  PO<sub>2</sub> cycle reduces the overall rate of H and OH recombination, gives positive sensitivities, and increases radical production in the flame. Thus, the HOPO + O  $\rightarrow$  HOPO<sub>2</sub> (Fig. 9a) reaction sends reactive flux to the less efficient cycle so it has as a positive sensitivity and promotes radical production. The same is true of the previously discussed  $PO_2$  +  $OH \rightarrow HOPO_2$  reaction. However, increasing the rate constant of the HOPO<sub>2</sub> + H  $\rightarrow$  PO<sub>2</sub> + H<sub>2</sub>O reaction returns flux to the more efficient HOPO  $\Leftrightarrow$  PO<sub>2</sub> cycle, gives a negative sensitivity, and inhibits radical production.

To gain further insights into the inhibition cycles, we schematically draw the pathways in Figs. 10a and 10b for the lean and rich flame, respectively.



Fig. 10. (a) Reaction pathway diagram for the key recombination pathways via phosphorus in lean flame. (b) Reaction pathway diagram for the key recombination pathways via phosphorus in rich flame.

Given in the figure are the reactions that have the greatest impact on the rate of production/destruction of H and OH along with their fluxes. Only cycles which have a flux greater than  $2 \times 10^{-6}$  mol/cm<sup>3</sup>/s are included. The fluxes are those present at 0.107 cm in the flame, which is the point of the greatest rate of production of PO<sub>2</sub>.

The two main inhibition cycles are:

$$PO_2 + H \rightarrow HOPO$$
 and  
 $HOPO + OH \rightarrow PO_2 + H_2O$ , (1)  
 $PO_2 + OH \rightarrow HOPO_2$  and

$$HOPO_2 + H \rightarrow PO_2 + H_2O.$$
 (2)

As can be seen in both cycles, the phosphorus compounds are acting catalytically to recombine H and OH to form H<sub>2</sub>O. Some H + H recombination between PO<sub>2</sub> and HOPO, as seen by MacDonald et al. [11] in a non-premixed flame, is also observed, but the H + OH and H + O recombination domi-

Table 2 Mole fraction of key  $PO_x H_y$  species in lean and rich flames

Species	Mole fraction (lean)	Mole fraction (rich)
PO	8.60e-6	4.37e-5
PO <sub>2</sub>	1.86e - 4	1.22e-4
PO <sub>3</sub>	3.13e-6	1.83e-7
HPO	1.75e-8	1.87e-7
HOPO	1.08e - 4	3.16e-4
HOPO <sub>2</sub>	2.57e-4	4.60e-5

Mole fractions at the location of the maximum rate of production for  $PO_2$  (distance from cold boundary = 0.107 cm) were used.

nates. Another reaction that is present, and part of the greater cycle, is HOPO +  $O \rightarrow HOPO_2$ .

In order to understand how the two inhibition cycles change with equivalence ratio, we need to examine how the oxidation state of key species changes in the rich versus the lean environment. If one were to consider the phosphorus species of interest to hold the form  $PO_xH_v$ , then it is expected, and has been shown [12] that in a lean flame, the more oxidized species, e.g., HOPO<sub>2</sub>, are in greater concentration than less oxidized species, e.g., HOPO. The reverse is true in the rich flame, where the concentration of HOPO is greater than HOPO<sub>2</sub>. The concentrations of these  $PO_x H_y$  species, evaluated at the point of maximum PO<sub>2</sub> rate of production (x = 0.107 cm) for the two flames are given in Table 2. The HPO concentration is insignificant and does not play a role in these flames.

As a result of the different concentrations, the relative importance of the two cycles varies, depending on the stoichiometry. Although for both flames the most important cycle is (1), this cycle is approximately 30% more important in the rich flame, where HOPO is more prevalent, than in the lean flame. Similarly in the rich flame, PO is playing a significant role, while for the lean flame, the corresponding species is PO<sub>3</sub>. In the lean flame, cycle (2) is about five times more significant due to the much higher concentration HOPO<sub>2</sub>. Also, because of this relatively high concentration, the alternate route through  $PO(OH)_2$ becomes important. Again, all cycles are present in both flames, but if the value of the flux is below the threshold, the cycle is not shown.

It is interesting, considering the different emphasis on different cycles in the rich and lean flames, that the overall suppression effectiveness in the two cases is comparable. It appears that the phosphorus will take the most efficient route to inhibit the flame even though different cycles are not necessarily equally effective for radical recombination. The ability of phosphorus compounds to inhibit the flame is quite robust in this regard and potentially unique.

Another point of interest is that the inhibition reactions have their greatest activity in the fairly hightemperature region of the flame, >1600 K (corresponding to a position of  $\sim 0.09$  cm). In fact, below about 1300 K, the net rate of production of all key phosphorus radicals is negative. This hightemperature dependence is consistent with the initial decomposition of the parent species needing to occur prior to the production of the small phosphorus oxy-acids. As a point of reference, at 1300 K, about half of the DMMP has been consumed. In addition, PO(OH)<sub>3</sub> is produced in the early part of the flame, which then decomposes to the key phosphorus compounds at higher temperatures. Work by Rumminger et al. [25] has shown that an "ideal" inhibitor is most effective when active in the >1700 K region of a premixed flame. This observation can aid in explaining why the phosphorus compounds are significantly more effective than halons in inhibiting a flame [2,26].

## 5. Conclusions

To further the understanding of the role of organophosphorus compounds in flame suppression, a more accurate mechanism was developed. A new reaction pathway for the HOPO<sub>2</sub> + H = PO<sub>2</sub> + H<sub>2</sub>O reaction was found that considerably increased its reaction rate constant compared to literature values. This reaction exhibited the second highest sensitivity of the organophosphorus reactions under lean conditions. To test the new mechanism, a study of the flame suppression by one characteristic organophosphorus compound, namely dimethyl methylphosphonate, under a range of equivalence ratios (0.8-1.3) was performed experimentally and numerically. Good agreement exists between the experimental and the numerical results. In the experiments, no significant bias of the ability for the DMMP to suppress the flame was observed for the rich versus lean cases. When studied numerically, the mechanism by which the DMMP, or OPCs in general, acts under different equivalence ratios can be explored. Although the same key catalytic cycles are observed for both equivalence ratios,  $\phi = 0.8$  and  $\phi = 1.3$ , the bias toward more highly oxidized species is seen in the lean case. This bias leads to the HOPO<sub>2</sub>  $\Leftrightarrow$  PO<sub>2</sub> inhibition cycle being more important in the lean than rich case. In the computations, the HOPO<sub>2</sub>  $\Leftrightarrow$  PO<sub>2</sub> inhibition cycle was found to be a less efficient than the HOPO  $\Leftrightarrow$  PO<sub>2</sub> cycle. This result leads to DMMP being less effective on the lean side than on the rich side in the computations. Even with this difference, the ability for the OPCs to be similarly effective under a range of equivalence ratios demonstrates their robustness as flame inhibitors.

In addition, OPCs similarity to the "ideal" inhibitor described by Rumminger et al. [25] in operating in the high-temperature region of the flame gives further understanding to their high level of effectiveness.

## Acknowledgments

The authors thank Dr. P.A. Glaude for helpful discussions on the reaction mechanism. The computational portions of this work were supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, and performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory, under Contract No. W-7405-Eng-48. The experimental part of this work was carried out with support from the Civilian Research and Development Foundation under Grant RC1-2386-NO-02 and by U.S. Army Research Office under Grant DAAD 19-00-1-0136, Modification No. P00001. Dr. Henry Curran acknowledges support from Enterprise Ireland under their Research Scholarship and International Collaboration Programmes.

### References

- J.W. Hastie, D.W. Bonnell, Molecular Chemistry of Inhibited Combustion Systems, National Bureau of Standards, NBSIR 80-2169, 1980.
- [2] M.A. MacDonald, T.M. Jayaweera, E.M. Fisher, F.C. Gouldin, Combust. Flame 116 (1999) 166–176.
- [3] J.E. Siow, N.M. Laurendeau, Combust. Flame 136 (2004) 16–24.
- [4] A. Twarowski, Combust. Flame 94 (1993) 91-107.
- [5] A. Twarowski, Combust. Flame 94 (1993) 341-348.
- [6] A. Twarowski, Combust. Flame 102 (1–2) (1995) 41– 54.
- [7] O.P. Korobeinichev, S.B. Ilyin, V.V. Mokrushin, A.G. Shmakov, Combust. Sci. Technol. 116 (1996) 51–67.
- [8] O.P. Korobeinichev, A.L. Mamaev, V.V. Sokolov, T.A. Bolshova, V.M. Schvartsberg, in: Proceedings of the Halon Option Technical Working Conference (HOTWC), Albuquerque, NM, 2001, pp. 173–186.
- [9] C.K. Westbrook, Proc. Combust. Inst. 19 (1983) 127– 141.
- [10] C.K. Westbrook, Combust. Sci. Technol. 34 (1983) 201–225.
- [11] M.A. MacDonald, E.M. Fisher, F.C. Gouldin, Combust. Flame 124 (4) (2001) 668–683.
- [12] O.P. Korobeinichev, V.M. Shvartsberg, A.G. Shmakov, T.A. Bolshova, T.M. Jayaweera, C.F. Melius, W.J. Pitz, C.K. Westbrook, Proc. Combust. Inst. 30 (2004) 2350– 2357.
- [13] G.T. Linteris, G.T. Truett, Combust. Flame 105 (1–2) (1996) 15–27.
- [14] H. Mache, A. Hebra, Sitzungsber. Osterreich. Akad. Wiss. Abt. (IIa) (1941) 150–157.
- [15] A. van Maaren, L.P.H. de Goey, Combust. Sci. Technol. 102 (1994) 309–314.

- [16] C.M. Vagelopoulos, F.N. Egolfopoulos, Proc. Combust. Inst. 25 (1994) 1341–1347.
- [17] I.V. Dyakov, A.A. Konnov, J. de Ruyck, K.J. Bosschaart, E.C.M. Brock, L.P.H. de Goey, Combust. Sci. Technol. 172 (2001) 81–96.
- [18] J.C. Mackie, G.B. Bacskay, N.L. Haworth, J. Phys. Chem. A 106 (2002) 10825–10830.
- [19] C.Y. Sheng, J.W. Bozzelli, J. Am. Chem. Soc. A 106 (2002) 7276–7293.
- [20] W. Tsang, J.T. Herron, J. Phys. Chem. Ref. Data 20 (1991) 609–663.
- [21] R.J. Kee, F.M. Rupley, J.A. Miller, M.E. Coltrin, J.F. Grcar, E. Meeks, H.K. Moffat, A.E. Lutz, G. Dixon-Lewis, M.D. Smooke, J. Warnatz, G.H. Evans, R.S. Larson, R.E. Mitchell, L.R. Petzold, W.C. Reynolds, M. Caracotsios, W.E. Stewart, P. Glarborg, C. Wang, O. Adigun, W.G. Houf, C.P. Chou, S.F. Miller, Chemkin Collection, 3.7.1, Reaction Design, Inc., San Diego, CA, 2003.
- [22] H.J. Curran, T.M. Jayaweera, W.J. Pitz, C.K. Westbrook, A Detailed Modeling Study of Propane Oxidation, Western States Section of the Combustion Institute, Davis, CA, 2004, Paper No. 04S-58.
- [23] C.M. Vagelopoulos, F.N. Egolfopoulos, Proc. Combust. Inst. 27 (1998) 513–519.
- [24] http://www-cms.llnl.gov/combustion/ combustion\_home.html.
- [25] M.D. Rumminger, V. Babushok, G.T. Linteris, Proc. Combust. Inst. 29 (2003) 329–336.
- [26] V.I. Babushok, W. Tsang, G.T. Linteris, D. Reinelt, Combust. Flame 115 (4) (1998) 551–560.
- [27] P.A. Glaude, H.J. Curran, W.J. Pitz, C.K. Westbrook, Proc. Combust. Inst. 28 (2000) 1749–1756.
- [28] W. Tsang, R.F. Hampson, J. Phys. Chem. Ref. Data 15 (1986) 1087.

- [29] N. Marinov, Int. J. Chem. Kinet. 31 (1999) 183-220.
- [30] T. Ingham, R.W. Walker, R.E. Woolford, Proc. Combust. Inst. 25 (1994) 767–774.
- [31] W. Tsang, J. Phys. Chem. Ref. Data 16 (3) (1987) 471– 508.
- [32] R. Atkinson, Int. J. Chem. Kinet. 18 (1986) 555-568.
- [33] J. Werner, T. Cool, Combust. Flame 117 (1–2) (1999) 78–98.
- [34] R.T. Wainner, K.L. McNesby, A.W. Daniel, A.W. Miziolek, V.I. Babushok, in: Halon Options Technical Working Conference (HOTWC), Albuquerque, NM, 2000, pp. 141–153.
- [35] W.B. DeMore, S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, M.J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling. Evaluation number 12, Jet Propulsion Laboratory, JPL, 1997, Publication 97-4.
- [36] J. Warnatz, in: W.C.J. Gardiner (Ed.), Combustion Chemistry, Springer-Verlag, New York, 1998, p. 509.
- [37] M. Evans, M. Polanyi, Trans. Faraday Soc. 34 (1938) 11.
- [38] K. Glaenzer, J. Troe, Ber. Bunsen-Ges. Phys. Chem. 78 (1974) 182.
- [39] C. Canosa, R.-D. Penzhorn, C. von Sonntag, Ber. Bunsen-Ges. Phys. Chem. 83 (1979) 217.
- [40] J.C. Mackie, G.B. Bacskay, N.L. Haworth, J. Phys. Chem. A 106 (2002) 10825–10830.
- [41] C. Melius, M.D. Allendorf, J. Phys. Chem. A 104 (11) (2000) 2168–2177.
- [42] C. Melius, in: S.N. Bulusu (Ed.), Chemistry and Physics of Energetic Materials, Kluwer Academic, Dordrecht, 1990, p. 21.
- [43] C. Melius, http://z.ca.sandia.gov/~melius/.