ISSN 1990-7931, Russian Journal of Physical Chemistry B, 2008, Vol. 2, No. 6, pp. 856–875. © Pleiades Publishing, Ltd., 2008. Original Russian Text © O.P. Korobeinichev, V.M. Shvartsberg, A.G. Shmakov, 2008, published in Khimicheskaya Fizika, 2008, Vol. 27, No. 11, pp. 5–27.

COMBUSTION AND EXPLOSION

Destruction of Organophosphorus Compounds in Flames and Nonthermal Plasmas

O. P. Korobeinichev, V. M. Shvartsberg, and A. G. Shmakov

Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences, Institutskaya ul. 3, Novosibirsk, 630090 Russia

> *e-mail: korobein@kinetics.nsc.ru* Received August 29, 2006

Abstract—The available results of experimental and theoretical studies of the chemistry and mechanism of the destruction of organophosphorus compounds (OPCs) in a flame and corona discharge plasma are systematized. The experimental methods, instrumentation, and methodological approaches used in determining the flame structure and identifying the products of OPC destruction are described. The published kinetic models capable of describing the decomposition of OPCs and the mechanisms of the promoting and inhibiting action of OPCs on combustion are considered. Common and distinctive features of the mechanisms of OPC destruction in various processes are examined. Practical aspects of the processed studied, including toxic waste disposal, chemical weapon elimination, and fire safety problems, are briefly overviewed.

DOI: 10.1134/S1990793108060031

1. INTRODUCTION

Interest in the chemistry of combustion of organophosphorus compounds (OPCs) is associated with their role in the incineration of toxic wastes (pesticides) and chemical warfare agents, such as sarin (OPCs are its simulants) and with their use as flame inhibitors, polymer combustion retardants, and catalysts in ramjet engines. The structural formulas of OPCs known as sarin simulants are listed in Table 1.

This review focuses on studies of the chemical mechanism of the destruction of OPCs in flames and nonthermal plasmas, largely performed at the Laboratory of Combustion Kinetics of the Institute of Chemical Kinetics and Combustion of the Siberian Division of the Russian Academy of Sciences over a period from 1990 to 2005.

An effective technology of destruction of toxic chemical wastes and other hazardous substances, including chemical warfare agents (CWAs), is incineration [1, 2]. This technology is pivotal in the program of destruction of CWAs accepted in the USA and is successfully realized at the Johnston Atoll [1]. In Russia, the incineration technology was realized at a KUASI mobile installation [3, 4], which is intended for the destruction of damaged chemical ammunition under field conditions. This technology is based on the twostage process: the detoxication of sarin and soman with diethanolamine with subsequent incineration of the product. Despite the development of alternative destruction methods, incineration remains the most promising one. The technology of destruction of CWAs by incineration was demonstrated in the USA at the Johnston Atoll. However, these activities were temporary stopped because of public concerns about ecological problems.

The ecological safety of incineration required the performance of research aimed at better understanding of the chemical mechanisms underlying the process of incineration. In this connection, a program for studying the mechanism of combustion of CWA simulants was launched in the USA, manned by scientists from the Cornel University, National Institute of Standards and Technology, Sandia Laboratory (USA), and the Laboratory of Kinetics of Combustion Processes of the Insti-

Compound	Structural formula		
Sarin	OCH(CH ₃) ₂ CH ₃ —P=O F		
Diisopropyl methyl- phosphonate (DIMP)	$CH_{3} - P = O$ $OCH(CH_{3})_{2}$ $OCH(CH_{3})_{2}$		
Dimethyl methylphos- phonate (DMMP)	OCH ₃ CH ₃ -P=O OCH ₃		
Trimethyl phosphate (TMP)	$CH_{3}O-P=O$ $OCH_{3}O-P=O$ $OCH_{3}O-P=O$ $OCH_{3}O-P=O$		

 Table 1. Structural formulas of sarin and its organophosphorus simulants

tute of Chemical Kinetics and Combustion of the Siberian Division of the Russian Academy of Sciences (Novosibirsk). This team developed the first kinetic model of the combustion of OPC simulants of CWAs. Studying the mechanism of the combustion of OPCs is also of considerable interest for flame extinction [5], for catalyzing hydrogen combustion in ramjet engines [6], and for suppressing the combustibility of polymers [7]. Organophosphorus compounds are promising substitutes of halons, the use of which was prohibited by the Montreal Protocol in 1978 because of their damaging effect on the ozone layer.

The development of a safe and efficient technology of incineration of CWAs is impossible without a deep understanding of the destruction of their simulants and without working out a kinetic model capable of describing this process. The history of studying the gasphase combustion of phosphorus probably dates back to the works of Khariton, Koval'skii, and Semenov [8– 10], who investigated the flammability limits of phosphorus vapor. The results were used by Academician Semenov in developing his theory of branched chain reactions.

In the present review, we will also consider the destruction of OPCs in a corona discharge plasma. This method is effective in purification of air from pollutant emissions of the chemical industries. The destruction of OPCs in a corona discharge cannot be used for creating a self-sufficient technology for destroying hazardous substances, but it may prove highly efficient at the second (afterburning) stage in order to decrease the trace concentrations of CWAs in air and industrial emissions still further.

According to [11], based on the results of competitive certification, the Russian regulatory bodies selected three technologies for the destruction of CWAs as the only legitimate for use at the territory of the Russian Federation, more specifically, two-stage technology, thermal method (also known as marten method), and one-stage procedure for destruction of CWAs immediately in the ammunition container (catalytic destruction method), as a standby variant. Note that the chemical mechanisms underlying the Russian technologies are fairly well understood and, obviously, require no additional fundamental research.

2. EXPERIMENTAL METHODS AND APPROACHES

2.1. Flame Structure

Knowledge of the chemistry and mechanism of combustion at the molecular level makes it possible to create combustion models capable of predicting many combustion characteristics important for practice, such as the rate and completeness of combustion, temperature and composition of the products under various conditions, and also to control the process of combustion by means of selecting conditions that would ensure the required characteristics of combustion.

The flame structure is the main source of information on the chemistry of combustion. One of the most effective method for studying the flame structure is probe mass spectrometry, a versatile method capable of (1) identifying the components present in the flame, (2) determining their quantitative composition (concentrations), and (3) measuring these concentrations in the combustion zone (examine the structure of these flames).

An efficient approach to studying combustion chemistry is to combine experimental methods with numerical simulations within the framework of a detailed kinetic mechanism. This combination makes it possible not only to understand the chemical mechanism of the process, but also to develop a kinetic model and constantly refine it by comparing its predictions with experimental data. At present, this approach is widely used in combustion research, in particular, it was applied to studying the chemistry of combustion of OPCs.

The most efficient method for determining the chemical structure of flames is the probe molecularbeam mass spectrometry (MBMS) with soft ionization, a technique that makes it possible to detect atoms, radicals, and labile components in the flame. It was successfully applied to studying the combustion of OPCs at the Cornel University (USA) [12] and at the Institute of Chemical Kinetics and Combustion of the Siberian Division of the Russian Academy of Sciences [13].

2.1.1. Molecular beam mass spectrometry. The best way to analyze the combustion products in situ is to use molecular beam sampling from the flame with the help of a sonic probe that forms a supersonic outflow of products into vacuum, which, passing through a skimmer, transforms into a molecular beam. The expansion of the products quenches chemical reactions in the sample. The skimmer cuts out the central part of the flow, free from the products of possible heterogeneous catalytic reactions on the internal walls of the probe. The composition of the molecular beam is analyzed by a soft-ionization mass spectrometry. The molecular beam method ensures the preservation of the sample during extraction and transport to the analyzer. Mass spectrometry makes it possible to simultaneously detect in situ all the product present in the flame, a capability inaccessible to any other method. Sampling is accomplished with a quartz probe attached to a stainless steel flange cooled with water. To conduct measurements in different zones of the flame, the burner was moved along its axis with respect to the immobile probe. The cathetometer accurately measured the position of the burner in the combustion chamber with respect to the probe.

Figure 1 shows the setup with molecular beam mass spectrometric sampling; for details, see [13]. The com-



Fig. 1. Schematic of the MBMS setup for sampling gaseous flames seeded with OPCs.

position and concentrations of gaseous species in the flame were measured with a MS-7302 quadrupole mass spectrometer equipped with a refined ion source with a small electron energy scatter ($\pm 0.25 \text{ eV}$), on the order of the thermal energy at the cathode temperature. The probe made of quartz had a shape of a cone with a height of 20–25 mm, an internal apex angle of 40°, a wall thickness near the apex of 0.05–0.08 mm, and an inlet orifice diameter of 0.05–0.2 mm.

To study the destruction of OPCs in flames, we used a hydrogen–oxygen flame, the structure of which was well studied both experimentally and theoretically [14]. The simplicity of the H₂–O₂–Ar flame (Ar is an inert diluent) and small number of components in it makes it convenient for analyzing the products and gaining insights into the mechanism of destruction of OPCs in such a flame. A premixed H₂–O₂–Ar flame of stoichiometric composition (0.26 : 0.13 : 0.61) was stabilized at a pressure of 43–80 torr over a Botha–Spalding flat burner [15] with a diameter of 24 or 40 mm and a temperature of 95°C.

The basic difference between the MBMS setups used in Russia and the USA consisted in the mode of

ionization of the molecular beam. At Cornel University, the molecular beam was ionized by VUV light with a quantum energy of 10.5 eV (118 nm). The ions obtained were detected with a time-of-flight mass spectrometer. Varying the emission wavelength of one of the dye lasers, it was possible to smoothly change the wavelength of ionizing radiation. VUV radiation was generated by tripling the third harmonics of a Nd-AYG laser (355 nm) in a cell filled with Xe.

The setup at the Institute of Chemical Kinetics and Combustion of the Siberian Division of the Russian Academy of Sciences employed soft electron-impact ionization (7–20 eV) with a small electron energy scatter followed by ion separation in a quadrupole mass spectrometer. The low scatter of electron energies was achieved by using cathode voltage-drop compensation [16]. This technique makes it possible to eliminate or, at least, decrease the fragmentation of ions, an effect that interferes with measurements of the concentrations of atoms, radicals, and other labile compounds. Table 2 lists the ionization potentials and ionizing voltages used by the authors to measure the mass spectra of atoms, free radicals, and basic OPCs. The ionization potentials of PO, PO₂, HOPO, HOPO₂, and (HO)₃PO were determined by measuring the ionization efficiency curves during direct sampling of flames seeded with OPCs (Fig. 2). The accuracy of measuring the ionization potentials is determined by the ionizing electron energy scatter, signal-to-noise ratio, and intensity of the signal itself. To select the optimal ionizing voltage when the appearance potentials of fragmentation ions are unknown is an arduous problem. Figure 2 shows the ionization efficiency curves for peaks with mass-tocharge ratios of 47 (PO), 63 (PO₂), and 64 (HOPO). As can be seen, the curves exhibit kinks, which are indicative of the emergence of contributions from fragmentation ions of other compounds. The existence of kinks is one of the criteria of selecting the required ionizing voltage.

Another specific feature of this setup is the mode of recording of mass spectra. The molecular beam formed from the sampled combustion products is modulated with a rotating disk with slits; i.e., when the beam path is opened, both background and molecular beam species contribute to the total signal, otherwise only background ones. Subtracting the second signal from the first one yields the molecular beam signal. Mass spectra are measured in the ion counting regime, a technique that makes it possible to eliminate interferences and increase the signal-to-noise ratio.

The test flames were also sampled using the microprobe method [17] with subsequent analysis of the products on a gas-liquid chromatograph. Since many of the extracted products of the destruction of OPCs are acids, they were preliminary silylated (the H atom of the OH group of the OPC was replaced by the trimethylsilyl group [18]). Although the microprobe method cannot detect active and unstable species in the combustion products, it allows one to identify the stable intermediate organophosphorus products of dimethylmethyl phosponate (DMMP) destruction [19].

FTIR spectroscopy was also used in combination with microprobe sampling to analyze the composition of flames, largely volatile and gaseous combustion products [19].

2.1.2. Microthermocouple measurements of the flame temperature. The temperature profiles in flames were measured with Pt/Pt + 10% Rh thermocouples 0.05 mm in diameter. The ends of the thermocouple were welded to a 0.2-mm-diameter wire fabricated from the same material. Springs provided a steady stretching of the thermocouple and made it possible to prevent it from being deformed in the flame [13]. Upon welding the surface of the thermocouple was coated with SiO₂ or Ceramobond 569 [20] to prevent catalytic processes. The corrections for thermal emission were estimated using the formula from [21]. To take into account the thermal disturbances introduced into the flame by the probe, the temperature profile across the flame was measured with a thermocouple the junction of which positioned at a distance of 0.25–0.30 mm from the probe end face.

2.2. Methods for Measuring the Laminar Flame Speed

The laminar flame speed was measured on a Mache–Hebra burner (a modification of the Bunsen burner). The burner appears as a quartz tube with a converging nozzle at the end. Such a nozzle is needed to make the visible flame contour take the shape of a regular cone. The laminar flame speed was calculated from the measured flow rate of the combustible mixture and the surface area of the flame cone. The size of the flame cone was identified with its luminescent contour. The error in determination of the flame speed by this method is $\pm 5\%$ (for stoichiometric methane–air flame).

The laminar flame speed was also measured by using the heat flux method [22, 23], which makes it possible to determine this parameter with a high accuracy ($\pm 1\%$ for a stoichiometric methane–air flame) over a wide range of compositions of the combustible mixture. The flat burner was a copper disk with small orifices; thermocouples were welded into orifices at various distances from the burner axis. The temperature of the disk was 60°C, whereas the combustible mixture temperature was 35°C. While passing through the orifices, the mixture was heated. By varying the flow rate of the combustible mixture, it is possible to achieve a uniform radial distribution of temperature over the disk surface, a situation that corresponds to the equality of the heat flux from the flame to the burner surface. In this case, the conditions of combustion are close to adiabatic. This means that the velocity of the combustible mixture equals the laminar flame speed.

Table 2. Mass-to-charge ratio, measured ionization potential, and the energy of ionizing electrons for the basic labile components of flames seeded with OPCs

Flame contaminants	m/z	Ionization potential, eV	Energy of ionizing electrons in expe- riment, eV
РО	47	8.3 ± 0.3	12.8
PO ₂	63	11 ± 0.5	12.8
HOPO	64	10.7 ± 0.3	12.8
HOPO ₂	80	12.4 ± 0.2	14.5
(HO) ₃ PO	98	11.5 ± 0.5	17.5
DMMP	124	9.9 ± 0.5	20.0
TMP	140	9.9 ± 0.5	20.0
Н	1	13.3 ± 0.5	16.2
0	16	13.6 ± 0.2	16.2
OH	17	13.2 ± 0.2	16.2

2.3. Simulation of the Structure and Speed of a Laminar Flame

The simulation of the flame structure was performed using the PREMIX and CHEMKIN-II computer codes [24, 25], which make it possible to calculate the concentration profiles of species in a flame stabilized over a flat burner and the laminar flame speed by using a detailed mechanism composed of elementary chemical reactions and databases of thermodynamic and transport properties. Due to the existence of the heat fluxes



Fig. 2. Ionization efficiency curves measured by sampling a 47-torr hydrogen–oxygen flame seeded with 0.2% TMP: (1) PO (m/z = 47), (2) PO₂ (m/z = 63), (3) HOPO (m/z = 64).

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Compound	BAC-MP4 [36], 2000	2000 CBS [37], 1999 BAC-G2 [40], 2004		G3X2 [38], 2002	
РО	-388.8	-32.6	-36.9	-37.6	
PO ₂	-282.6	-293.9	-298.0	-290.9	
PO ₃	-429.7	-449.4	-449.4		
НОРО	-451.4	-469.8	-467.3	-469.4	
HOPO ₂	-689.7	-716.5	-718.5	-712.7	
PO(OH) ₂	-646.6		-660.0	-663.8	
HPO	-75.2	-94.5	-96.1		
HPO ₂	-405.9		-424.3		
P_2O_3	-615.3		-657.1		
P_2O_4	-854.0		-907.1		
P ₂ O ₅	-1070.9		-1134.0		

Table 3. Enthalpy of formation ΔH_f^0 of phosphorus-containing compounds (kJ/mol) calculated by various quantum-chemical methods

from the flame to the sampler and burner, notably at atmospheric pressure, the flame structure was calculated employing the experimentally measured temperature profile. For this purpose, as in [26], we used the data obtained with the help of a thermocouple located near the inlet orifice of the probe.

The simplest mechanism of methane oxidation included 58 reactions and 20 species. Of these reactions, 23 belong to the hydrogen oxidation mechanism. This set of reactions was successfully used in modeling the structure of a stoichiometric hydrogen–oxygen flame stabilized over a flat burner at a pressure of 47 torr [14, 26–28] and of lean methane–oxygen flame stabilized at 76 torr [29, 30].

The structure and laminar flame speed of methaneoxygen flames at atmospheric pressure was calculated using the GRI 3.0 mechanism [31], composed of 325 reactions involving 53 species. The structure of propane-oxygen flames was simulated using 469 reactions involving 77 species [32, 33].

The structure of hydrogen-oxygen flames seeded with trimethyl phosphate (TMP) and DMMP was determined using a kinetic model of OPCs destruction in flames composed of 35 steps. This model was initially developed using experimental data on the structure of flames seeded with DMMP [12, 13], thermochemical data obtained by Melius, and the mechanism proposed by Twarowski [6, 34, 35]; it was tested by comparing the experimental and theoretical results on the structure of H₂-O₂-Ar flames seeded with TMP and DMMP [27–29] at a pressure of 47 torr and methane–oxygen flames seeded with TMP at 76 torr [29]. This model includes the mechanism developed by Twarowski [6, 34, 35] with modified rate constants from [28]. Later, the model was refined by altering the rate constants of six key steps and was successfully applied to calculating the structure of flames at atmospheric pressure.

The enthalpies of formation of phosphorus oxyacids were calculated by various quantum-chemical methods [36–38] (Table 3). At the same time, the enthalpies of formation of some activated complexes were calculated by varying their structures (intermediate states) for different routes of the key reactions. As a result, it was found that some of the steps in the mechanism of the destruction of OPCs are nonelementary, consisting of a sequence of elementary transformations [39, 40]. Based on the calculations performed, the authors of [39, 40] developed a more detailed mechanism of the destruction of OPCs, which, in addition, was capable of describing propane–air mixtures of various compositions at atmospheric pressure. This mechanism consists of 210 reactions and 41 phosphorus-containing species.

3. CHEMISTRY OF COMBUSTION OF OPCS

3.1. Destruction of OPCs in Flames

The first works that shed light on the destruction of OPCs in flames are obviously [41, 13, 12], published in 1994, 1996, and 1999, respectively. In these studies, the soft ionization MBMS method was used to measure the profiles of the intensity of mass peaks belonging to the combustion products of TMP, tributyl phosphate (TBP), and DMMP in hydrogen-oxygen flames at 80 and 50 torr. In [41], based on the concentration profiles of TMP and TBP in a flame, the authors demonstrated that OPCs added to a low-pressure hydrogen-oxygen flame are consumed faster than the main components $(H_2 \text{ and } O_2)$. In addition, it was established that, upon subtracting the contribution from TMP, the m/z = 110peak intensity profile has two characteristic maxima. The authors assumed that this profile belongs to the $C_2H_7O_3P^+$ ions identified as $(CH_3O)_2(H)PO$ (dimethyl phosphite) or $(CH_3O)_3P$. In the same work, [41], the intensity profiles of the mass peaks at m/z = 47 (PO), $48 (\text{HPO}), 63 (\text{PO}_2), 64 (\text{HOPO}), \text{ and } 80 (\text{HOPO}_2)$



Fig. 3. Flow diagram for the transformation of DMMP in a low-pressure flame proposed in [13].

were also recorded. Thus, the final phosphorus-containing and intermediate products of TMP destruction in flames were identified.

3.1.1. Mechanism of DMMP destruction. In [13], the structure of hydrogen–oxygen flames seeded with DMMP at 47 and 76 torr were studied. The most important result of this study is the detection of a key products of DMMP destruction with m/z = 110 and 94, which were identified with methyl methylphosphonate ((CH₃O)(HO)(CH₃)PO) and methylphosphonic acid ((HO)₂(CH₃)PO), respectively. The mass peaks belonging to the final phosphorus-containing products of DMMP destruction, PO, PO₂, HOPO, and HOPO₂, were also recorded. The identified products made it possible to propose a pioneering mechanism of DMMP destruction in flames, a flow diagram of which is displayed in Fig. 3. Later, this mechanism was refined.

Thus, in [13, 41] an overall mechanism of transformations of OPCs in flames was formulated. It was demonstrated that the destruction of OPCs occurs via the substitution of H and OH for CH₃ and CH₃O groups. In addition, in these studies, a complete set of final phosphorus-containing products of the combustion of OPCs was identified. The data obtained made it possible to develop models of the destruction of OPCs in flames capable of predicting the structure and speed of such flames.

The authors of [13] examined the effect of DMMP additives on the structure of hydrogen–oxygen flames. These data constituted the basis for studying the promoting and inhibiting effects of OPCs on combustion.

One of the first and most detailed studies of the chemistry and mechanism of the destruction of OPCs in flames was undertaken by Werner and Cool [12], who examined the chemical structure of a rich hydrogen–oxygen–DMMP (0.1 vol %) flame and, based on the data obtained, proposed a kinetic scheme of DMMP destruction in flames. What is more, a number of intermediate products of DMMP destruction, CH_3PO_2 (78), CH_3OPO (78), $(CH_3)(CH_3O)(OCH_2)PO$ (123), $(OH)_2(CH_3)PO$ (94), and $P(OH)(CH_3)(OCH_3)_2$ (110)

(masses are indicated in parentheses), were detected in [12]. In another study, the same authors determined the ionization potentials of CH₃PO₂ and CH₃OPO₂ [42]. It was experimentally demonstrated that the destruction of OPCs occurs through their interaction with H and OH, more specifically, the substitution of OH for alkyl and alkoxyl groups. The authors of [42] calculated the rate constant for the thermal destruction of DMMP, which is characterized by an activation energy of 365 kJ/mol, a value indicative of a small contribution from pyrolysis to the consumption of DMMP during combustion. Unfortunately, no measurements of the absolute concentrations of phosphorus-containing combustion products were performed in [42]; instead, calibration against the calculated profiles at maxima was performed. This circumstance somewhat downgrades the importance of this study, since the authors were unable to test the proposed model of the flame structure.

The data on the behavior of the above compounds in flames seeded with DMMP were used by a number of authors to develop their own models for the destruction of DMMP in flames and simulate the chemical structure and speed of laminar flames seeded with DMMP [26, 42, 43].

The next step in understanding the chemistry of combustion of OPCs involved quantitative measurements of the concentrations of phosphorus-containing combustion products, which made it possible to test and refine the models of the process [44]. Since the concentrations of PO, PO₂, HOPO, and HOPO₂, short-lived compounds, cannot be calibrated directly, their calibration coefficients were determined from material balance for phosphorus. The exception is HOPO₂ (mataphosphoric acid), which exists in the form of crystal hydrates of composition $(P_2O_5)_x(H_2O)_y$ (x : y \approx 1 : 1), but it has a vapor pressure too low to perform direct calibration. To determine the sensitivity coefficients, the authors measured the intensity of mass peaks at m/z =40 (Ar), 47 (PO), 63 (PO₂), 64 (HOPO), and 80 (HOPO₂) in the final products of hydrogen-oxygen flames with

No.	Reaction	<i>A</i> _T [6]	A _{mod} [28]	п	E
1	OH + PO + M = HOPO + M	1.19×10^{20}	1.19×10^{20}	-1.8	5.82
2	$H + HOPO = H_2O + PO$	3.16×10^{13}	6.32×10^{11}	0	49.95
3	$OH + PO_2 + M = HOPO_2 + M$	1.60×10^{24}	1.60×10^{25}	-2.3	1.19
4	$H + HOPO_2 = H_2O + PO_2$	3.16×10^{13}	6.32×10^{11}	0	49.95
5	$H + PO_2 + M = HOPO + M$	9.73×10^{23}	9.73×10^{24}	-2.0	2.70
6	$OH + HOPO = H_2O + PO_2$	3.16×10^{11}	3.16×10^{11}	0	0
7	$H + HOPO = H_2 + PO$	3.16×10^{13}	7.90×10^{11}	0	0.18
8	$O + HOPO = OH + PO_2$	3.16×10^{13}	$1.58 imes 10^{12}$	0	0
9	$OH + PO = H + PO_2$	3.16×10^{11}	6.32×10^{10}	0	24.95
10	$O + PO + M = PO_2 + M$	2.36×10^{23}	2.36×10^{24}	-2.1	4.63
11	$O_2 + PO = O + PO_2$	3.16×10^{11}	3.16×10^{10}	0	23.95
12	$OH + HOPO = H + HOPO_2$	3.16×10^{11}	6.32×10^{10}	0	40.70
13	$O + HOPO + M = HOPO_2 + M$	1.59×10^{24}	7.95×10^{24}	-2.1	4.17
14	$O + HOPO_2 = O_2 + HOPO$	3.16×10^{13}	6.23×10^{11}	0	34.48
15	$PO + HPO_2 = PO_2 + HOPO$	3.16×10^{11}	3.16×10^{11}	0	40.78

Table 4. Comparison of the rate constants for the key reactions estimated by Twarowski (A_T) and modified by the authors of [28] ($k = AT^n \exp(-E/RT)$)

Note: In cm³, mol, s, and kJ units.

DMMP and TMP additives in various concentrations. The sensitivity coefficients $k_{\rm PO}$, $k_{\rm PO_2}$, $k_{\rm HOPO}$, and $k_{\rm HOPO_2}$ were determined using the singular value decomposition [45] of the system of linear equations $\Sigma(k_i I_i^j / I_{40}^j) =$ $\alpha^{j}/\alpha^{j}_{Ar}$, where k_{i} is the calibration coefficient for the *i*th compound, I_i^j is the intensity of the parent peak of the *i*th compound in the *j*th flame, and α^{j} is the initial mole fraction of TMP (or DMMP) in the *j*th flame. The computer code took into account the root-mean-square errors in measuring the intensities of the peaks and made it possible to determine the accuracy of calculation of the sensitivity coefficients. The introduction of additional equations into the system (it was deliberately overspecified) by measuring the intensities of peaks in flames of other compositions increased the accuracy of calculations. The calculated calibration coefficients made it possible to measure the concentration profiles of PO, PO2, HOPO, and HOPO2 in an hydrogen-oxygen-DMMP flame stabilized over a flat burner at a pressure of 47 torr.

Modeling the structure of this flame with the use of the mechanism proposed by Twarowski demonstrated that, at the rate constant used in this mechanism, the experimentally measured concentrations of these component cannot be predicted correctly. An analysis of the sensitivity of the reactions in Twarowski's mechanism to the concentrations of phosphorus oxides and phosphorus acids (Table 4) showed than the theoretical results can be matched to the experimental data by increasing the rate constants of trimolecular reactions 1, 3, 5, 10, and 13 in Table 4 and decrease the rate constants of bimolecular reactions 2, 4, 7, 8, 9, 11, 12, and 14. These changes in the rate constants entailed an increase in the calculated concentration of HOPO₂ and a decrease in that of PO. In addition, as a result, of the above changes, the calculated (HOPO)/(PO₂) ratio became closer to the experimental value.

In [12, 13], the mechanism of DMMP destruction was extended to include several primary stages of DMMP destruction with the formation of (CH₃)PO(OH)(OCH₃) (m/z = 110), PO(OH)(OCH₃)₂ (m/z = 126), CH₃P(OH)(OCH₃)₂ (m/z = 125), and (CH₃PO(OCH₃)(OCH₂)) (m/z = 123). The reactions involving CH₃P(OH)(OCH₃)₂ (m/z = 125) were not included into the final version of the model, since an analysis of the sensitivity of DMMP consumption to these reactions demonstrated that their influence was negligibly small.

In addition, these measurements demonstrated that the flame contained considerable concentrations of (CH₃)PO(OH)(OCH₃), whereas PO(OH)(OCH₃)₂ (m/z =126) and CH₃PO(OCH₃)(OCH₂) (m/z = 123) were not detected at all. Therefore, the authors of [28] suggested that the main route of DMMP destruction consists of the reactions

DMMP + H (or OH) = $(CH_3)PO(OH)(OCH_3)$ + CH_3 (or OCH₃), $(CH_3)PO(OH)(OCH_3) + H$ (or OH) = $(CH_3)PO(OH)_2 + CH_3$ (or OCH₃), $(CH_3)PO(OH)_2 + OH = PO(OH)_3 + CH_3$, $PO(OH)_3 \longrightarrow final products$.



Fig. 4. Flow diagram for the destruction of DMMP in flames proposed in [28].

The assumption that the interaction of DMMP with OH mainly yields methyl methylphosphonate, rather than dimethyl phosphate is supported by the fact that the dissociation energy of the C–O bond is smaller than that of the C–P bond. The reaction mechanism of DMMP destruction from [28] is displayed in Fig. 4.

The proposed mechanism of DMMP destruction in flames was used to calculate the structure of flames in mixtures containing 0.2% DMMP. A comparison with the experimental results showed a satisfactory agreement for most components. In particular, the paper [28] features the concentration profiles of the following intermediate products of DMMP destruction in flames: methyl metaphosphate (CH₃OPO₂), methyl methylphosphonate, methylphosphonic acid, and orthophosphoric acid. No direct calibration for the organophosphorus products of DMMP destruction was performed because of their instability or low volatility (methylphosphonic acid). To obtain the concentration profiles of these compounds in the flame, we equated the concentrations at the maxima of the calculated and measured profiles, as was done in [12].

A team from the Cornel University observed a wide variety of stable phosphorus-containing products of DMMP destruction by using microprobe sampling from a lean methane-oxygen flame seeded with DMMP at a pressure of 660-670 torr with subsequent gas-liquid chromatographic analysis [17]. In particular, the following products of DMMP combustion were detected: methyl methylphosphonate ($(CH_3O)(OH)(CH_3)PO$), dimethyl phosphate ((CH₃O)₂(OH)PO), phosphonic monomethyl phosphate acid $((HO)_2(H)PO),$ $((CH_3O)(OH)_2PO)$, and orthophosphoric acid $((HO)_3PO)$. Although the concentrations of these compounds were not determined, this study confirmed the correctness of the identification of the DMMP combustion products in [12, 13, 28] and extended their number.

An important result of measuring the structure of flames seeded with OPCs is that, despite distinctions in the structure of DMMP, TMP, and diisopropyl methylphosphonate (DIMP), the composition of the final phosphorus-containing products is essentially the same. It depends on the properties of the flame itself, such as the temperature and equivalence ratio, rather than on the structure of the initial OPC. Note that PO, PO_2 , HOPO, and HOPO₂ are formed in the flame at a high temperature, but after cooling, the composition of the combustion products changes substantially, probably shifting to a complex mixture of phosphorus acids.

3.1.2. Mechanism of TMP destruction. In contrast to DMMP, the mechanism of destruction of TMP in flames has been studied and worked out more extensively and has been tested under a variety of conditions. To determine the concentration profiles of organophosphorus products of TMP destruction, direct calibrations for TMP, dimethyl phosphate ((CH₃O)₂(HO)PO), and dimethyl phosphite ((CH₃O)₂(H)PO) were performed [27]. To synthesize pure methyl monoesters of orthophosphoric acid proved difficult, and, therefore, their concentrations were estimated from the material balance for phosphorus.

In addition, the steps of transformations of TMP, which logically follow from the composition of its combustion products, the authors took into account the reaction of TMP with OH, the products of which proved to be not dimethyl phosphate and methanol, as it was believed earlier, but water and a organophosphorus radical [46]:

 $(CH_3O)_3PO + OH = (CH_2O)(CH_3O)_2PO + H_2O,$ $\Delta H_{298}^{\circ} = 79.09 \text{ kJ/mol.}$

The rate constant of this reaction was measured at 300 K without determining the activation energy [46]. The activation energy of this reaction was set equal to that of an analogous reaction, DMMP with OH [12], i.e., 16.7 kJ/mol. The preexponential factor was calculated based on the accepted value of the activation energy and the measured rate constant [46]. Thus, this reaction was included into the reaction scheme as one of the possible primary steps of TMP destruction in flames.

A flow diagram of TMP destruction is shown in Fig. 5 [27, 28]. It is interesting to perform an integral analysis of the routes of TMP destruction and a number of products of its incomplete decomposition (Fig. 6). As can be seen, the formation of ($^{\circ}CH_2O$)(CH_3O)₂PO is a key step, with most of the products being formed through this reaction. More than 70% of TMP is consumed by this reaction. The proposed mechanism of TMP destruction was used for modeling the structure of a H_2 – O_2 –Ar flame seeded with TMP.

Figure 7 shows the measured and calculated final temperature of a H_2 -O₂-Ar flame stabilized over a flat burner at a pressure of 47 torr as functions of the added TMP concentration. As can be seen, the experimental and theoretical results are in satisfactory agreement, an observation indicative of the self-consistency of the

proposed model. For comparison, Fig. 7 also shows the equilibrium temperatures for the adiabatic flames of the same compositions. The difference in the temperature between the adiabatic and stabilized flames can be accounted for by the fact that a considerable fraction of heat released is absorbed by the burner. That the temperature rises with the TMP concentration can be explained not by the introduction of additional fuel but by the ability of OPC combustion products to promote combustion by catalyzing the recombination of radicals. This property of OPCs is illustrated in Fig. 8, which shows the concentration profiles of the stable components, H₂, O₂, and H₂O, in a H₂-O₂-Ar flame with (0.2%) and without TMP stabilized at 47 torr. That the combustion zone width narrows and completeness of combustion increases is indicative of a promoting effect of TPM on the flame. This effect initially grows with the OPC concentration, passing through a maximum at 0.5–0.6 vol %. Figure 9 shows the calculated dependence of the laminar flame speed of an H₂–O₂–Ar flame seeded with TMP on the TMP concentration at a pressure of 47 torr. At concentrations of up to 0.6%, TMP acts as a prompter, but at higher concentrations, it inhibits the flame. At a pressure of 1 atm, TMP acts only as an inhibitor, why is explained below (section 3.2). The effect of OPCs on the concentrations of radicals in the flame is demonstrated in Fig. 10, which displays the calculated and measured concentration profiles of H, O, and OH in a H_2 – O_2 –Ar flame with (0.2%) and without TMP. The flame was stabilized over a flat burner at a pressure of 47 torr. The effect of OPCs on the concentrations of radicals is the most important property of these compounds. The data presented show that the calculation results nearly coincide with the experimental data.

Figure 11 displays the measured and calculated concentration profiles of TMP and intermediate organophosphorus products of its decomposition in a H_2 – O_2 –Ar flame at a low pressure. A comparison of the experimental and theoretical results shows that, despite certain deviations, the model satisfactorily predicts the concentration profiles of the decomposition products of the initial compound. Figure 12 shows calculated and measured concentration profiles of the final phosphorus-containing products of TMP combustion (PO, PO₂, HOPO, HOPO₂, and (HO)₃PO). As can be seen, the calculation and experimental results are in satisfactory agreement. As can be concluded from the results of a series of studies on the chemistry of combustion of OPCs, the requirement that a kinetic model would satisfactorily predict the distribution of PO, PO₂, HOPO, and HOPO₂ concentrations in flames is most exacting. Nevertheless, it is this criterion that, in combination with the ability to predict the concentration profiles of atoms and radicals, makes it possible to assess the efficiency of a mechanism in modeling the combustion of OPCs, an aspect especially important in describing the properties of OPCs as inhibitors and promoters.



Fig. 5. Flow diagram for the destruction of TMP and intermediate products in flames.

When modeling the structure of a methane–oxygen flame at a pressure of 1 atm and calculating its speed as a function of the OPC concentration with the use of the mechanism applied to describing a low-pressure flame, the authors of [47] revealed discrepancies with the experimental data, both in the concentration profiles of phosphorus oxides and phosphorus acids and in the dependence of the laminar flame speed on the TMP concentration. An analysis of the sensitivity of the laminar flame speed to the rate constant of the reactions involving PO, PO₂, HOPO, and HOPO₂ and of the effect of these reactions on the concentrations of phosphorus-containing products suggested that the preexponential factors of the rate constants for a number of key reactions, a total of eight (Table 4), should be changed.

3.1.3. DIMP destruction mechanism. In addition to the destruction of TMP and DMMP [27, 28], the chemistry of combustion of DIMP in a low-pressure H_2/O_2 flame was also studied [48]. In contrast to TMP and DMMP, DIMP is relatively easily pyrolyzed in an inert gas flow. In [49], its pyrolysis in a flow reactor was

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studied and the rate constant of this process was determined:

DIMP + M \longrightarrow isopropyl methyl phosphate + C₃H₆ (+82.3 kJ/mol), $k = 10^{12} \exp\{(-153.4 \pm 20)/RT\}, \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$

Therefore, the DIMP destruction mechanism was to be extended to include the reactions of its thermal decomposition. However, estimating the contribution of this step to the overall rate of decomposition of the initial compound, the authors of [48] concluded that the thermal decomposition plays a minor role in the general mechanism. As with the other OPCs, the main steps in DIMP destruction are the reactions of this molecule with H and OH, which result in the replacement of CH_3 and C_3H_7O groups by H or OH. The authors of [48] also proposed the possible steps in the destruction of sarin, by analogy with the DIMP destruction mechanism; a total of 10 reactions, for which the heat effects was estimated based on the thermochemical data quantumchemically calculated by Melius.



Fig. 6. Relative contributions (in %) from the main routes of consumption of TMP and some organophosphorus products of its destruction in a 47-torr hydrogen–oxygen flame.

An important stage in the development of the mechanism of combustion of OPCs and relevant kinetic model of the process constitute theoretical works performed at the Lawrence Livermore National Laboratory (USA). The development of the model was based on quantum-chemical calculations of the thermochemical properties of phosphorus-containing molecules and transition states [40, 50], as well as the rate constants. From the kinetic point of view, this approach is more substantiated than a simple adjustment of rate constants by variation, as was done at the initial stage of the studies. The values of the enthalpy, entropy, and heat capacity for 25 compounds of pentavalent phosphorus, in which the phosphorus atom is bonded to hydrogen, carbon, nitrogen, and sulfur atoms, were calculated. In this



Fig. 7. Dependence of the final temperature of a hydrogen– oxygen flame stabilized over a flat burner at a pressure of 47 torr on the TMP additive concentration: (\bigcirc) measurements, (line) simulation results, and (\bigcirc) calculated adiabatic temperature.

way, the authors of [36] calculated the rate constants of the unimolecular decomposition of dimethyl ethylphosphonate, triethyl phosphate, and DIMP. The correctness of calculation of the rate constants for the decomposition of these OPCs was checked by comparing the calculation results with the experimental data on pyrolysis in a flow reactor [36]. In addition, the authors of [36] proposed mechanisms of destruction of DMMP and TMP in flames on the basis of a detailed kinetic scheme. These authors claimed that they took into account all possible intermediate products of OPC destruction. The proposed models were successfully applied to simulating the structure of low-pressure H_2-O_2 flames seeded with 0.2% DMMP or TMP. A comparison of the calculation results with the experimental data from [27, 28] demonstrated good agreement not only for the concentration profiles of stable compounds (H_2, O_2, H_2O) in the flame but also for the concentration profiles of PO, PO₂, HOPO, HOPO₂, and (HO)₃PO, a criterion most difficult to satisfy. Note that, at that time, the proposed mechanism was most comprehensive, composed of 202 reactions for 41 phosphorus-containing species. Note that the simulations of the experimentally measured structure of subatmospheric CH_4 – O_2 flames revealed no advantages of this mechanism over the previous one, despite a substantially different number of stages, the method for determining the rate constants [50], and the difference between the rate constants at 1700 K for the key steps (1, 2, 7, and 8 in Table 5) of both models.

Later, the same authors developed mechanisms of destruction of OPCs and fluorinated OPCs [51], including TMP, DMMP, DIMP, and sarin. The hierarchical reaction schemes were created based on the earlier mechanisms of the destruction of OPCs with the use of the bond additivity rule. The kinetic models of the combustion of the above OPCs and sarin were used to predict the rates of their consumption in a well-stirred

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Fig. 8. Effect of a 0.2% TMP additive (lower plot) on the concentration profiles of the stable components of a hydrogen–oxygen flame stabilized over a flat burner at a pressure of 47 torr; the points and lines are the experimental and simulation results, respectively.

reactor in an air-natural gas (94% methane and 6% ethane) mixture, a process that imitates their incineration. A comparison of the dependences of the concentrations of OPCs in the combustion products on the temperature and time of residence in the reactor demonstrated that the behavior of TMP is identical to that of DMMP and sarin, whereas the dependences for DIMP and sarin coincide completely. Based on these observations, the authors concluded that only DIMP can be considered an imitator of sarin. Figure 13 shows simplified flow diagrams for the thermal destruction of DIMP and sarin in a well-stirred reactor at a high temperature. Note that the destruction mechanism cannot be reduced to the thermal decomposition stages. The paper also contains a complete mechanism of sarin combustion composed of 24 reactions, including interaction with radicals. A comparative analysis of the mechanism of destruction of OPCs demonstrated that the six-center reaction of C_3H_6 elimination involved in



Fig. 9. Dependence of the speed of hydrogen–oxygen–TMP flame on the initial concentration of TMP at (I) 47 and (2) 760 torr.

the thermal decomposition of DIMP and sarin is responsible for their reactivity being higher than that of TMP and DMMP. Note that the conclusions drawn by the authors contradict the results of an earlier work [48], where the mechanism of DIMP destruction in a low-pressure H₂–O₂ flame was studied both experimentally and theoretically. According to [48], the thermal decomposition of DIMP gives only a minor contribution to the overall rate of its destruction. This may be attributed to the fact that a low-pressure hydrogen-oxygen flame contains large concentrations of atoms and radicals (according to [14], the total mole fraction of O, H, and OH is about 0.1), and, therefore, the contribution from thermal decomposition is small. Under actual conditions excitant during incineration of CWAs (~1 atm), thermal decomposition obviously plays a more important role.

3.2. Mechanism of Inhibition (Promotion) of Flames by OPC Additives

One of the most interesting results concerning the destruction of OPCs in flames is the promoting and inhibiting effects of these compounds on combustion. How OPCs affect the characteristics flames is a separate problem, which will be touched upon only briefly in the present review because of volume limitations. We are planning to write a special review on this subject. Hastie and Bonnell [5], pioneers in studying the chemistry of combustion of OPCs, studied the effect of TMP on atmospheric-pressure methane-oxygen and hydrogen-oxygen flames of various types and compositions by using MBMS and optical and spectroscopic methods. Based on visual observations of the flame cone height, they revealed that the introduction of TMP results in a decrease in the speed of a methane-oxygen laminar flame and were the first to propose several reac-



Fig. 10. Effect of a 0.2% TMP additive on the concentration of H, O, and OH in a hydrogen-oxygen flame stabilized over a flat burner at a pressure of 47 torr; the points and lines are the experimental and simulation results, respectively.

tions that described the inhibition of methane–oxygen flames by phosphorus-containing compounds.

Studies of the mechanism of influence of OPCs on the rate of recombination of H and OH in flames were greatly contributed by Twarowski [6, 35, 36], who experimentally demonstrated that, at a temperature near 2000 K, the phosphine combustion products stimulate the recombination of H and OH radicals. Twarowski assumed that this process is catalyzed by phosphorus oxides and acids (PO, PO₂, HOPO, and HOPO₂) and proposed a mechanism of catalytic recombination with the participation of these compounds.

That the combustion zone narrows and the final temperature increases when a low-pressure (47 torr) hydrogen–oxygen flame is seeded with OPCs was first observed in [13, 14] (Fig. 8). This effect was termed promoting. It was found that OPC additives strongly affect the concentrations of atoms and radicals. Calcu-



Fig. 11. Concentration profiles of TMP and intermediate product organophosphorus products of its destruction in a hydrogen-oxygen–TMP (0.2%) flame stabilized over a flat burner at a pressure of 47 torr; the points and lines are the experimental and simulation results, respectively.

lations of the normal burning velocity of an H₂–O₂–Ar flame at 47 torr demonstrated that it increases with the concentration of added TMP, passing through a maximum at 0.6% TMP (Fig. 9). These calculations also revealed that, at atmospheric pressure, TMP acts on such flames as an inhibitor [29]. The effect observed by the authors, that the flame speed increases while the concentrations of radicals decrease upon introduction of OPC into the flame, seems to be a unique phenomenon. It has been commonly accepted that a decrease in the concentration of radicals is associated with the inhibition of combustion, i.e., a decrease in the flame speed and an increase in the combustion zone. Such an effect was produced by OPC on the flame at atmospheric pressure. It is interesting that the same processes are responsible for inhibition and promotion. A more detailed explanation of the nature of this effect will be given below.

An analysis of the sensitivity of the laminar flame speed to the rate constants of the key reactions in the hydrogen oxidation mechanism (without phosphorus) demonstrated [52, 53] that, at various concentrations of TMP, only the rate constant of the chain-branching step $H + O_2 = OH + O$ influences the normal burning velocity of the TMP-seeded flame. That the rate of this reaction increases with the OPC concentration can be explained by the increase in the rate constant of this reaction caused by the temperature rise (the activation energy is E = 61.9 kJ/mol) associated with the catalytically enhanced recombination of H and OH. This explanation of the effects of promotion and inhibition of H_2-O_2 flames by OPC additives is consistent with Zel'dovich's theory of hydrogen–oxygen flames [54], according to which recombination reactions simultaneously retard the chain process (chain termination) and promote it via heat release. At a small concentration of the additive, the increase in the rate of the chainbranching reaction overrides that in the rate of the chain-termination reaction, thereby enhancing the laminar flame speed. At a high concentration of the additive, when the adiabatic combustion temperature is achieved, the chain-termination rate exceeds the chainbranching rate, and, therefore, the flame speed decreases as the additive concentration is increased still further. It was established that, in contrast to hydrogenoxygen flames, TMP additives to methane-oxygen flames act as an inhibitor.

Note that the properties of OPCs as inhibitors and flame suppressants have been studied rather extensively. The effect of OPCs on the flame speed and on the degree of extinction flame stretching was studied and the minimum quenching concentrations of a number of compounds were determined.

A significant contribution to understanding and refining the mechanism of inhibition of OPC-containing flames was made in [40, 41]. In this works, the structure and speed of propane–oxygen and propane-air flames of various compositions were measured and calculated; in addition, the thermochemical properties of Mole fraction (×100) 0.16 0.14 0.12 0.10 0.08



Fig. 12. Concentration profiles of (\bigcirc) PO, (\spadesuit) PO₂, (\Box) HOPO, (\blacktriangle) HOPO₂, and (\blacktriangledown) (HO)₃PO in a 47-torr hydrogen-oxygen–TMP (0.2%) flame stabilized over a flat burner; the points and lines are the experimental and simulation results, respectively.

phosphorus-containing compounds and the potential energy surfaces for the key catalytic recombination reactions were calculated by new quantum-chemical methods. The calculations demonstrated that a number of stages previously considered elementary occur, in fact, in three steps (Fig. 14). The introduction of an additional stage of intramolecular rearrangement resulted in a decrease in the activation energy by more than 16 kJ/mol. At 1500 K, this is equivalent to an increase in the reaction rate by more than an order of magnitude.

The proposed model was used to calculate the structure of lean and rich propane–oxygen flames stabilized over a flat burner at atmospheric pressure [40]. The speed of laminar propane flames of various compositions at atmospheric pressure were also calculated [41].

No	Reaction	[29]			[36]		
110.		Α	п	Ε	Α	п	Ε
1	$OH + PO_2 + M = HOPO_2 + M$	1.6×10^{24}	-2.3	1.19	3.2×10^{25}	-2.3	1.19
2	$H + HOPO_2 = H_2O + PO_2$	6.32×10^{12}	0	49.87	—	-	—
3	$H + PO_2 + M = HOPO + M$	9.73×10^{24}	-2.0	2.70	1.46×10^{25}	-2.0	2.70
4	$OH + HOPO = H_2O + PO_2$	3.16×10^{12}	0	0	1.2×10^{6}	2.0	-6.27
5	$H + HOPO = H_2 + PO_2$	$7.9 imes 10^{11}$	0	0.18	6.8×10^{13}	0	33.86
6	$O + HOPO = OH + PO_2$	1.58×10^{13}	0	0	1.0×10^{13}	0	0
7	$O + HOPO + M = HOPO_2 + M$	1.3×10^{23}	-2.1	4.16	1.2×10^{27}	-3.0	8.53
8	$O + HOPO_2 = O_2 + HOPO$	6.32×10^{12}	0	34.43	5.0×10^{12}	0	62.7

Table 5. Rate constants for the eight key reactions in two models of OPC destruction ($k = AT^n \exp(-E/RT)$)

Note: In cm³, mol, s, and kJ units.



Fig. 13. Comparison of the mechanisms of destruction of DIMP (left) and sarin (right) at atmospheric pressure proposed in [51].

At the same time, MBMS measurements of the characteristics of TMP-seeded (0.12 vol %) lean (with an equivalence ratio of $\phi = 0.8$) and rich ($\phi = 1.2$) C₃H₈–O₂–Ar flames stabilized at atmospheric pressure were performed. Of greatest interest are the concentration profiles of phosphorus oxides and acids. It was found that, as ϕ increases from 0.8 to 1.2, the composition of PO, PO₂, HOPO, and HOPO₂ changes significantly. It was demonstrated that, while the main component in the lean flame is HOPO₂ (more than 80%) (high degree of oxidation of phosphorus), that in the lean flame is



Fig. 14. Potential energy surfaces for the possible reactions between $HOPO_2$ and H and some products thereof as calculated by quantum-chemical methods. The numerals denote the standard enthalpies of formation of compounds and transition states (kcal/mol).

HOPO (lower degree of oxidation). The developed model was applied to modeling the structure of lean and rich propane–oxygen flames seeded with 0.12% TMP. A comparison of the calculation and experimental results showed that this model closely describes the concentration profiles of the stable components (C₃H₈, O₂, H₂O, and CO₂). The agreement for PO, PO₂, HOPO, and HOPO₂ in the lean flame was also satisfactory. The calculated and measured values of the speed of C₃H₈–air laminar flames at $\phi = 0.8$ –1.3 with and with DMMP additive are also in good agreement [41]. The proposed mechanism can be used for describing the structure and speed of propane–oxygen laminar flames seeded with OPCs.

4. CHEMISTRY OF DESTRUCTION OF OPCS IN A CORONA DISCHARGE PLASMA

Despite the recent progress in studying the physical and chemical characteristics of the destruction of hazardous substance in a corona discharge plasma [55], there remains a lot of problems to be solved. Up to now, the destruction of OPCs in the corona discharge has remained practically unstudied. The available publications on the subject [56–58] contain no data on the kinetics and mechanism of the destruction of OPCs in the corona discharge. In the current work, we presented and systematized the results of detailed studies on the kinetics and mechanism of the destruction of DMMP, DIMP, and TMP (compounds belonging to phosphates and phophonates) conducted at the Laboratory of Kinetics of Combustion Processes of the Institute of



Fig. 15. Schematic of the experimental setup for studying the destruction of OPCs in a nonthermal corona discharge plasma.

Chemical Kinetics and Combustion of the Siberian Division of the Russian Academy of Sciences in cooperation with the New Jersey Institute of Technology (USA) [59–61].

For many volatile organic compounds (VOCs), the results obtained obeyed to the $X/X_0 = \exp(-KP/FX_0)$ law, where X and X_0 are the current and initial mole fractions of OPC, P is active power consumed by the reactor, F is the volumetric flow rate of the gas passing through the reactor, and K is the rate constant of the process. This led the authors of [55] to conclude that the ionic mechanism is largely responsible for the destruction of a number of VOCs. Therefore, it was interesting to check whether this law is valid for OPCs.

4.1. Experimental Method

Experiments on the destruction of OPCs in a nonthermal plasma were performed on the setup depicted in Fig. 15. It consists of a reactor connected to a MBMS unit for analyzing gaseous destruction products and to liquid-nitrogen traps and aerosol filters for capturing phosphorus-containing decomposition products. The corona discharge reactor was a quartz tube with two electrodes: a wire coaxially fixed inside and an external braid over the tube. The central electrode was fed with a 12 kV alternating voltage (50 Hz). OPC vapor diluted in a carrier gas was passed through the reactor. The carrier gases were helium, argon, nitrogen, or dry air. The mole fraction of OPC in the flow was varied from 5×10^{-5} to 5×10^{-4} . The active power consumed by the reactor was measured using the method proposed in [56]. The volatile decomposition products were analyzed on the MBMS setup [13]. The nonvolatile phosphorus-containing products of OPC decomposition were analyzed on a chromatomass spectrometer with preliminary silylization [18].

4.2. Kinetics and Mechanism of OPC Destruction in a Corona Discharge

It was demonstrated [59–61] that the decrease in the concentration of the initial substance depends not only on the active (in contrast to reactive) power absorbed by the reactor but also by the initial OPC concentration in the carrier gas flow and the flow rate of the carrier gas itself. It was also established that the active power is



Fig. 16. Semilogarithmic dependence of the relative decrease in the concentrations of various OPCs on the parameter *E* at K = 160: (\bullet) TMP, (\blacksquare) DIMP, (\blacktriangle) DMMP.

strongly dependent on the nature of the carrier gas; i.e., the higher the ionizability of the gas, the larger the power dissipated in the reactor, all other things being equal. The efficiency of OPC destruction increases with the ionization potential of the carrier gas, which decreases in the series helium > argon > nitrogen > oxygen. The authors of [55] proposed an approach based on the determination of the dependence of the kinetic characteristics of VOC destruction on the electric power consumed by the discharge. It was suggested to represent the data obtained in the $ln(X/X_0) - E_0$ coordinates, where X_0 and X are the concentrations of the initial VOC at the inlet and outlet of the reactor (ppm), $E_0 = KPF^{-1}X_0^{-1}$ (J cm⁻³ ppm⁻¹), P is the power consumed by the discharge (W), and F is the volumetric flow rate of the carrier gas (cm³/s). This approach was used to study the destruction of OPCs in a corona discharge. Figure 16 shows how the relative changes of the concentrations of various OPCs depend on the parameter E_0 . As can be seen, all experimental points lie on a single straight line in the $\log(X/X_0) - E_0$ coordinates. It was established that, at initial OPC concentrations of $C_0 = 500-20$ ppm, the relative concentration decrease X/X_0 due to the destruction process obeying the law $\log(X/X_0) = -KPF^{-1}X_0^{-1}$, where K is the destruction rate constant. The parameter $V = KPF^{-1}X_0^{-1}$ characterizes the destruction energy per OPC molecule. This means that, as the initial OPC concentration X_0 decreases, the energy spent on destruction does so proportionally. The destruction rate constant K being equal to 160 for all the OPCs studied suggests that the efficiencies of destruction of TMP, DMMP, and DIMP are identical. The physical meaning of the rate constant is the volumetric consumption of OPCs per unit power spent on destruction. It was revealed that (Fig. 17) the intermediate products of DMMP destruction in a corona discharge plasma are methyl methylphosphonate $((CH_3)(CH_3O)(OH)PO)$ and monomethyl phosphate ((CH₃O)(OH)₂PO). The final products were methylphosphonic ((HO)₂(CH₃)PO) and orthophosphoric $((HO)_3PO)$ acids. The same compounds are the final products of destruction of DIMP, whereas the intermediate destruction products are isopropyl methylphosphonate and methylphosphonic acid. The destruction of TMP yields dimethyl phosphate $((CH_3O)_2(OH)PO)$



Fig. 17. Normalize mole fraction of DMMP and products of its decomposition (MMP, methyl methylphosphonate; MPA, methylphosphonic acid, and OPA, orthophosphoric acid) in a nonthermal plasma as a function of the parameter *E*.

and monomethyl phosphate, as intermediates, and orthophosphoric acid, as a final product. An analysis of the products of destruction of OPCs showed that, despite essentially different conditions in the flame and plasma, OPCs experience similar transformations, which consist in the sequential substitution of H and OH for alkoxy and alkyl groups. Nevertheless, the mechanisms of destruction in plasmas and flames are evidently fundamentally different. The dependences obtained can obviously be interpreted within the framework of a mechanism based on ion-molecular rather than radical reactions. According to [61], the decomposition of an OPC molecule occurs in two stages: the molecule is ionized via charge transfer from a carrier gas molecular ion and then the OPC ion formed dissociate:

$$DIMP + O_2^+ \longrightarrow DIMP^+ + O_2,$$
$$DIMP^+ \longrightarrow IMP + C_3 H_6^+.$$

Although the second stage is essentially endothermic (+46 kJ/mol), the heat released by the first stage (\approx 570 kJ/mol) is more than enough to compensate for the heat consumed at the second stage; i.e., the overall process of destruction is exothermic.

It is somewhat disappointing that even the MBMS method did not permit the authors to identify active species involved or formed during the destruction of OPCs inside the reactor.

Note that the phosphorus-containing destruction products and the initial compound deposit onto the reactor walls, from where they a removed with a solvent for subsequent analysis. For low-volatile compounds, such as methylphosphonic and orthophosphoric acids, it is quite expected. Note, however, that even relatively volatile compounds deposit as well. According to [60], the gaseous products of OPC destruction are CO, CO_2 , and methane. This result suggests that such reactors are able not only to decrease the concentration of OPCs in the flow but also to trap phosphoruscontaining destruction products and unreacted initial OPCs, a factor that enhances the efficiency of this method and offers additional prospects for practical uses of this process.

5. CONCLUSIONS

Thus, we summarized and analyzed the published data on the chemistry and mechanism of the destruction of OPCs in flames and nonthermal plasmas. The use of modern experimental computational methods made it possible to examine the process of destruction of OPCs and develop a number of detailed kinetic models capable of predicting the concentration profiles of decomposition products across the flame front. A wide variety of compounds, including TMP, DMMP, DIMP, diethyl methylphosphonate, and sarin, were studied. While the early studies were performed with hydrogen–oxygen

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flames at low pressures, the subsequent investigations of the destruction of OPCs were conducted in hydrocarbon flames at atmospheric pressures.

A significant progress has been made in understanding the mechanisms of promotion and inhibition and in developing models describing the effect of OPCs on the structure and speed of flames. Of special interest is the discovery and explanation of promotion, a unique phenomenon. Interestingly, but the observation of the promoting effect of classical organophosphorus inhibitors initially created a great deal of distrust among experts in the field of combustion and chemical kinetics. They performed additional calculations to confirm the soundness of the previous results.

Note that the destruction of OPCs in nonthermal plasmas has received much lesser attention than their combustion; in particular, the mechanism and kinetic model of this process remain to be fragmentary.

The published data led us to the following conclusions. Despite the distinctions in the mechanism of the processes involved, flames and nonthermal plasmas are effective means of destruction of OPCs. While combustion is the standard method of disposal of CWAs, the use of corona discharge for purification of air and toxic emission is only a promising prospect. Despite extensive research work done, the combustion of OPCs has been studied predominantly in near-stoichiometric flames. Given that the chemistry of highly fuel-rich flames is more complicated than that of lean and stoichiometric flames, it makes sense to assume that the proposed models will be unable to correctly predict the structure of fuel-rich flames. For example, there is no reliable evidence whether OPCs can be formed in fuelrich flames from organic radicals and phosphorus oxides. Little is known about the mechanism of inhibition of rich hydrocarbon flames. It is reasonable to suppose that the composition of phosphorus-containing combustion products responsible for the catalytic recombination of radicals will be dependent on the fuel excess, a factor that can substantially affect the properties of OPCs as flame inhibitors.

ACKNOWLEDGMENTS

The works included in the review were supported by the Russian Foundation for Basic Research (project no. 97-03-32473a), U.S. Army Research Office (grant nos. DAAG55-97-1-407, DAAG55-98-1-0512, and DAAD19-00-1-0136), U.S. Civilian Research and Development Foundation (grant no. RC1-2386-NO-02), and INTAS (grant no. 03-51-4724).

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