

# Ignition Delay Time Measurements of Sarin Surrogate (TEP, DMMP)-Based Mixtures in a Heated Shock Tube

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## 1 Introduction

Over the past few years, chemical weapons of mass destruction (CWMD) such as Sarin ( $C_4H_{10}FO_2P$ ), a nerve agent, were used against civilians in the Middle East. To defeat a potential terrorist attack involving this kind of chemical warfare, the most likely scenario relies on the use of a conventional weapon with energetic material payload. However, very little is known on the high-temperature chemistry of Sarin, and it is possible that employing such a method to destroy it could actually exacerbate the CWMD problem, since the intermediate species and final products released could also be toxic. It is therefore important to understand the detailed combustion chemistry of Sarin over a wide range of conditions, to provide capabilities for eliminating the threat or, at least, to mitigate its effects.

Thus far, studies on the destruction of CWMD such as Sarin have only involved methods applicable to a controlled environment, like in the case of the planned destruction of stockpiles by incineration. Surrogates of Sarin are used in these studies, for obvious safety reasons, and one can mention experimental studies in flames [1-5] as well as numerical studies [6-9]. More experimental results are therefore needed to develop and validate detailed kinetics models for Sarin and its surrogates over a wide range of conditions. Although ignition delay time measurements in shock tubes provide well-characterized and accurate results to easily assess the overall reactivity of a model, this kind of measurement has never been undertaken so far for Sarin or any of its surrogates. The aim of the present study was therefore to measure ignition delay times ( $\tau_{ign}$ ) of various mixtures based on common Sarin surrogates, namely dimethyl methylphosphonate (DMMP,  $C_3H_9O_3P$ ) and tri-ethyl-phosphate (TEP,  $C_6H_{15}O_4P$ ). The structures of Sarin, DMMP, and TEP are visible in Fig. 1.

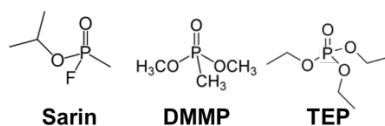


Figure 1. Structure of Sarin and the two surrogates considered in the present study

It is worth noting that DMMP is also a potential fire suppressant [5, 9], which explains the fact that a model based on the earlier work of Jayaweera et al. [4] was proposed recently by Babushok et al. [9]. However, there is no chemical model or experimental data available for TEP.

In this study, the ignition delay times of dilute mixtures containing either DMMP or TEP were measured in a shock tube to help in refining and developing these models. Mixtures of simulants and O<sub>2</sub> diluted in 99% Ar were investigated at 3 equivalence ratios ( $\phi$ ): 0.5, 1.0, and 2.0 for TEP and at  $\phi = 0.5$  only for DMMP. To assess the effect of the simulants on the combustion chemistry of hydrocarbons, mixtures of methane/oxygen diluted in Ar and seeded with DMMP or TEP were also investigated at the same 3 equivalence ratios. The amount of TEP added corresponded to 10% of the fuel concentration. Finally, a fuel lean mixture of H<sub>2</sub>/O<sub>2</sub> seeded with DMMP or TEP was also studied. The experimental setup and conditions investigated are presented first, followed by the presentation of the experimental results.

## 2 Experimental Setup

The shock tube utilized during this study is 6.1 meter long with a 4-m square (10.8-cm section) driven part. Both DMMP and TEP have low vapor pressures at room conditions, so the shock tube was heated to 50°C during this study. A detailed description of the shock tube and heating system can be found in Rotavera and Petersen [10]. During the experiment, the shock-front velocity was measured using four, high-frequency piezoelectric pressure transducers (PCB 113A) located toward the end of the shock tube. The time necessary for the shock wave to travel between two transducers was measured using 120-MHz counter/timers (Phillips P6666). Pressure and temperature behind the reflected shock waves were calculated using the determined incident shock wave velocity in conjunction with the 1-D shock relations and the initial conditions. Test pressure was monitored during the experiment by one PCB 134A transducer located at the endwall and one Kistler 603 B1 transducer located at the sidewall. In the same plane as the sidewall pressure transducer, two CaF<sub>2</sub> windows are mounted flush with the inner wall of the reactor. These windows allow for the observation of the light coming from the chemiluminescence emission from the  $A^2\Sigma^+ \rightarrow X^2\Pi$  transition of the excited-state hydroxyl radical (OH\*). The light was collected onto a photomultiplier tube (Hamamatsu 1P21) equipped with an interference filter (307 ± 10 nm).

Mixtures were prepared in a heated mixing tank using the partial pressure method. The fuel, Sarin simulants, and oxygen were introduced in the mixture using a 0-100 torr pressure gage while Ar was introduced using a 0-1000 torr pressure gage. Gages were purchased from MKS and are auto-regulated in temperature at 200°C. The vapor pressure of the Sarin simulants was kept at 1 torr or below during the mixtures' preparation. Note that 1 torr of DMMP at 50°C represents about 25% of its saturating vapor pressure at this condition (Butrow et al. [11]). Based on the same study, it can be estimated that 1 torr of TEP represents about 50% of its saturating vapor pressure at 50°C. It is assumed that no condensation of the surrogates occurred during the mixture preparation. The gases used during this study were all high purity (H<sub>2</sub> and CH<sub>4</sub> from Praxair, 99.999% and 99.97% purity, respectively, O<sub>2</sub> and Ar from Airgas 99.994% and 99.999%, respectively). TEP (≥99.8% purity) and DMMP (>97% purity) were purchased from Sigma Aldrich. The conditions investigated are visible in Table 1.

The mixtures of methane and H<sub>2</sub> seeded with DMMP or TEP were compared to neat mixtures (i.e. without Sarin surrogate) studied at similar conditions. These mixtures were recently explored by our group in a different shock tube [12,13]. Some repeat experiments with the neat mixtures and with the heated shock tube used herein were performed to successfully ensure that results were comparable and reproducible between the two experimental devices.

Table 1: Mixtures and conditions investigated during this study.

| Fuel (mole %) |                       | O <sub>2</sub> (mole %) | Ar (mole %) | Equiv. ratio ( $\phi$ ) | P <sub>5</sub> (atm) | T <sub>5</sub> (K) |
|---------------|-----------------------|-------------------------|-------------|-------------------------|----------------------|--------------------|
| 0.095 DMMP    |                       | 0.905                   | 99.00       | 0.5                     | 1.70±0.20            | 1315-1585          |
| 0.053 TEP     |                       | 0.947                   | 99.00       | 0.5                     | 1.70±0.10            | 1360-1665          |
| 0.10 TEP      |                       | 0.90                    | 99.00       | 1.0                     | 1.55±0.15            | 1340-1660          |
| 0.182 TEP     |                       | 0.818                   | 99.00       | 2.0                     | 1.60±0.10            | 1345-1750          |
| 0.1 DMMP      | 1.0 H <sub>2</sub>    | 1.0                     | 97.90       | 0.5                     | 1.75±0.10            | 1055-1470          |
| 0.10 TEP      | 1.0 H <sub>2</sub>    | 1.0                     | 97.90       | 0.5                     | 1.85±0.10            | 1130-1525          |
| 0.04 DMMP     | 0.40 CH <sub>4</sub>  | 1.60                    | 97.96       | 0.5                     | 1.45±0.20            | 1490-1915          |
| 0.067 DMMP    | 0.667 CH <sub>4</sub> | 1.333                   | 97.933      | 1.0                     | 1.50±0.15            | 1565-1925          |
| 0.10 DMMP     | 1.00 CH <sub>4</sub>  | 1.00                    | 97.90       | 2.0                     | 1.40±0.15            | 1665-2010          |
| 0.04 TEP      | 0.40 CH <sub>4</sub>  | 1.60                    | 97.96       | 0.5                     | 1.42±0.10            | 1575-2000          |
| 0.067 TEP     | 0.667 CH <sub>4</sub> | 1.333                   | 97.933      | 1.0                     | 1.40±0.15            | 1600-2120          |
| 0.10 TEP      | 1.00 CH <sub>4</sub>  | 1.00                    | 97.90       | 2.0                     | 1.40±0.15            | 1635-2025          |

### 3 Experimental results

While the typical OH\* profile for hydrocarbons exhibits a rise in OH\* after a delay time that varies with the temperature (the lower the temperature, the longer the delay time), the OH\* signal observed for the stimulants is different. For both DMMP and TEP, the OH\* signal rapidly rises after time zero, and the time observed before the appearance of the OH\* signal does not vary much with the temperature (Fig. 2). In this case, only the time at which the OH\* signal reaches its maximum,  $\tau_{\max}$ , varies significantly with the temperature. Interestingly, the shape of the OH\* profile is similar for DMMP and TEP, and this shape and  $\tau_{\max}$  do not seem to vary with the equivalence ratio for a given temperature, as per the TEP results. However, comparing  $\tau_{\max}$  for DMMP and TEP shows that the two surrogates have different reactivities. The ignition delay time is similar for both components on the low-temperature side, but  $\tau_{\max}$  for DMMP is shorter by a factor of almost 2 on the high-temperature side.

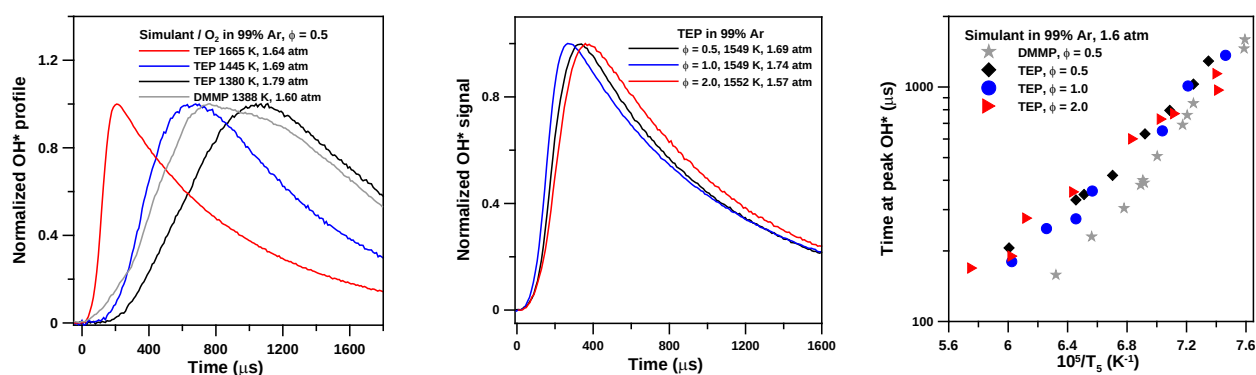


Figure 2. Left: comparison between normalized OH\* profiles for DMMP and TEP at  $\phi = 0.5$ ; center: comparison between normalized OH\* profiles for TEP at various  $\phi$  and around 1550 K; right: comparison between  $\tau_{\max}$  for DMMP and TEP.

Concerning the data where the stimulants were seeded into  $H_2$  and  $CH_4$  mixtures, the  $OH^*$  profiles exhibited the classical fashion described above. The ignition delay time was therefore determined using the method used in our former studies [12-13], as visible in Fig. 3.

The addition of a small fraction of DMMP or TEP to a  $H_2/O_2$  mixture induces some noticeable changes in the reactivity, as can be seen in Fig. 3 (right). In both cases, the overall activation energy is increased by the Sarin surrogates additions, in a larger proportion for TEP than for DMMP. This difference is probably due to the larger hydrocarbon moiety of TEP. The DMMP addition reduces the ignition delay time up to a factor of 2 at high temperature and tends to increase moderately  $\tau_{ign}$  above 1175 K. The increase in  $\tau_{ign}$  is more important when TEP is added since the ignition delay time is longer by a factor of almost 3 on the colder-temperature side. As for DMMP,  $\tau_{ign}$  is shorter on the higher-temperature side, by a factor of close to 2 for the highest temperature investigated.

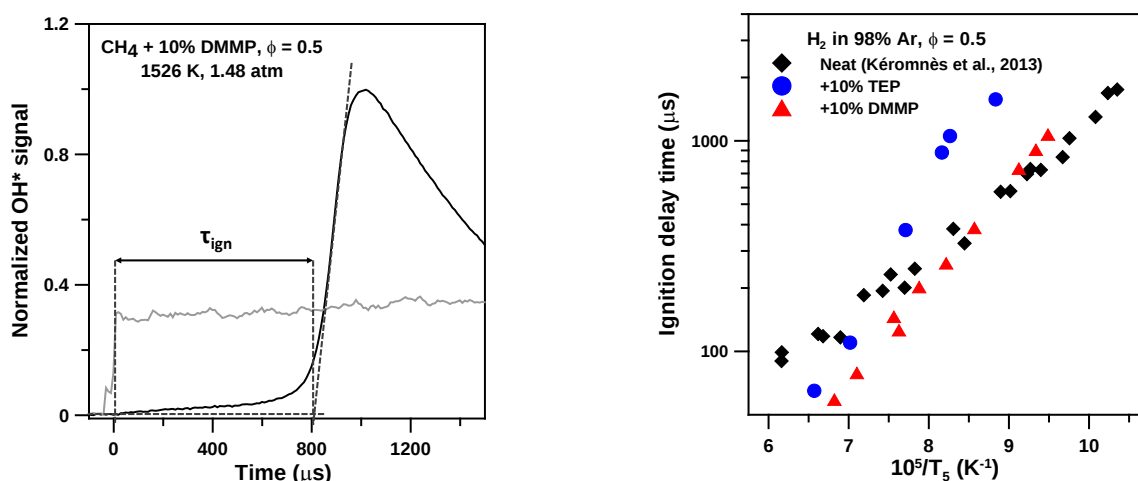


Figure 3. Left: method of determination of the ignition delay time for the mixtures containing  $H_2$  or  $CH_4$ , with or without DMMP or TEP addition; right: Effect of TEP and DMMP addition on a  $H_2/O_2$  mixture ( $\phi = 0.5$ ) around 1.7 atm. The concentration of the simulant is 10% of the  $H_2$  concentration (Ar concentration is changed accordingly).

The effect of DMMP and TEP addition on the ignition delay times of  $CH_4$  mixtures is visible in Fig. 4. As can be seen, the addition of any of this Sarin surrogate notably reduces  $\tau_{ign}$  for all conditions investigated, with DMMP having a larger effect than TEP except at  $\phi = 2.0$ , low temperature, where the two surrogates yield identical results. The  $\tau_{ign}$  reduction is also larger at low temperatures than at high temperatures. For the fuel lean case, the ignition delay time is reduced by a factor of between 3 (high temperature) and 4 (low temperature) with DMMP and by between 55% (low temperature) and 25% (high temperature) for TEP. Relatively similar numbers are found with TEP for the other equivalence ratios investigated, whereas the shortening in  $\tau_{ign}$  is dependent of the equivalence ratio for DMMP. For the stoichiometric mixture, ignition delay times are shortened by a factor of between 3.6 (low temperature) and 2.4 (high temperature), whereas these factors are only of around 2.1 and slightly below 2, respectively, for the fuel rich mixture.

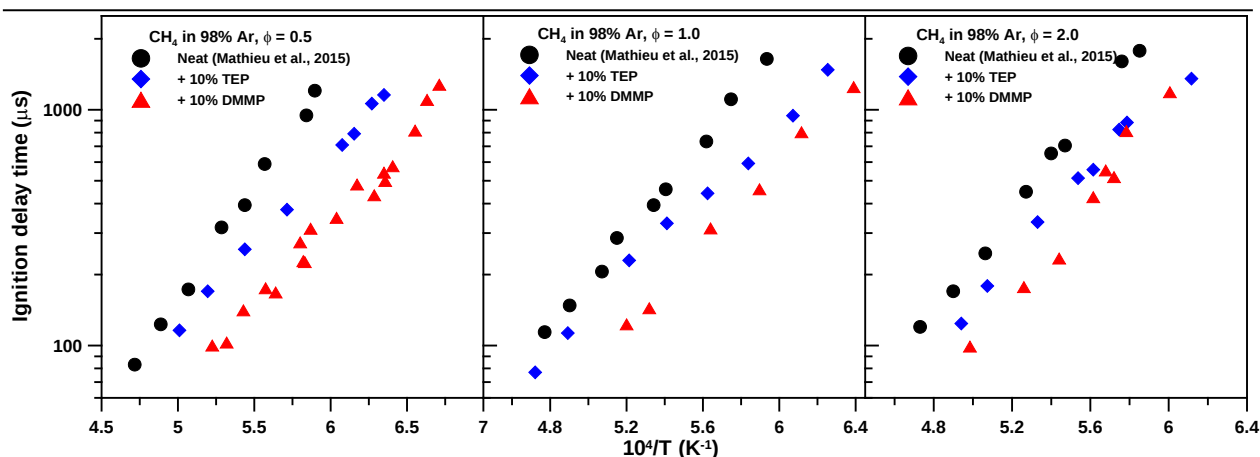


Figure 4. Effect of TEP and DMMP addition on a  $\text{CH}_4/\text{O}_2$  mixture at around 1.4 atm. Left:  $\phi = 0.5$ ; center:  $\phi = 1.0$ ; right:  $\phi = 2.0$ .

## 4 Conclusions

In this study, ignition delay times of two Sarin stimulants, namely dimethyl methylphosphonate (DMMP) and tri-ethyl-phosphate (TEP), were measured in a heated shock tube for the first time. These surrogates were studied alone or doped to methane or hydrogen mixtures. Results showed an unusual behavior on the  $\text{OH}^*$  profile when the stimulants were studied alone, where the appearance of the  $\text{OH}^*$  always occurred shortly after time zero and rise to a maximum that varies significantly with the temperature. When added to either  $\text{H}_2$  or  $\text{CH}_4$  mixtures, the  $\text{OH}^*$  profiles present the same behavior as for the neat mixtures, but the reactivity is changed noticeably in most cases.

The comparison between the two Sarin surrogates demonstrates stark differences in their reactivity, for all conditions and mixtures investigated. This difference shows that proposing an accurate combustion model for Sarin probably necessitates studying several Sarin surrogates; each Sarin simulant representing one part of the structure of Sarin. The data presented herein will be useful to validate and develop chemical kinetic models for DMMP and TEP, and once these models have been developed and validated on a common base, it will be possible to assemble with more confidence a detailed kinetics model for Sarin.

## 5 Acknowledgments

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## References

- [1] Korobeinichev OP, Ilyin SB, Shvartsberg VM, Chernov AA. (1999). The destruction chemistry of organophosphorus compounds in flames—I: quantitative determination of final phosphorus-containing species in hydrogen-oxygen flames. *Combust. Flame* 118: 718.

- [2] Korobeinichev OP, Ilyin SB, Bolshova TA, Shvartsberg VM, Chernov AA. (2000). The chemistry of the destruction of organophosphorus compounds in flames—III: the destruction of DMMP and TMP in a flame of hydrogen and oxygen. *Combust. Flame* 121: 593.
- [3] Korobeinichev OP, Chernov AA, Bolshova TA. (2000). The chemistry of the destruction of organophosphorus compounds in flames—IV: destruction of DIMP in a flame of  $H_2 + O_2 + Ar$ . *Combust. Flame* 123: 412.
- [4] Jayaweera TM, Fisher EM, Fleming JW. (2005). Flame suppression by aerosols derived from aqueous solutions containing phosphorus. *Combust. Flame* 141: 308.
- [5] Bouvet N, Linteris GT, Babushok VI, Takahashi F, Katta VR, Krämer R. (2016). A comparison of the gas-phase fire retardant action of DMMP and  $Br_2$  in co-flow diffusion flame extinguishment. *Combust. Flame* 169: 340.
- [6] Glaude P-A, Curran HJ, Pitz WJ, Westbrook CK. (2000). Kinetic study of the combustion of organophosphorus compounds. *Proc. Combust. Inst.* 28: 1749.
- [7] Glaude P-A, Melius C, Pitz WJ, Westbrook CK. (2002). Detailed chemical kinetic reaction mechanisms for incineration of organophosphorus and fluoroorganophosphorus compounds. *Proc. Combust. Inst.* 29: 2469.
- [8] Korobeinichev OP, Shvartsberg VM, Shmakov AG, Bolshova TA, Jayaweera TM, Melius CF, Pitz WJ, Westbrook CK, Curran HJ. (2005). Flame inhibition by phosphorus-containing compounds in lean and rich propane flames. *Proc. Combust. Inst.* 30: 2353.
- [9] Babushok VI, Linteris GT, Katta VR, Takahashi F. (2016). Influence of hydrocarbon moiety of DMMP on flame propagation in lean mixtures. *Combust. Flame* 171: 168.
- [10] Rotavera B, Petersen EL. (2013). Model predictions of higher-order normal alkane ignition from dilute shock-tube experiments. *Shock Waves* 23: 345.
- [11] Butrow AB, Buchanan JH, Tevault DE. (2009). Vapor Pressure of Organophosphorus Nerve Agent Simulant Compounds. *J. Chem. Engin. Data* 54: 1876.
- [12] Mathieu O, Goulier J, Gourmel F, Mannan MS, Chaumeix N, Petersen EL. (2015). Experimental study of the effect of  $CF_3I$  addition on the ignition delay time and laminar flame speed of methane, ethylene, and propane. *Proc. Combust. Inst.* 35: 2731.
- [13] Kéromnès A, Metcalfe WK, Heufer KA, Donohoe N, Das AK, Sung C-J, Herzler J, Naumann C, Griebel P, Mathieu O, Krejci MC, Petersen EL, Pitz WJ, Curran HJ. (2013). An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures. *Combust. Flame* 160: 995.