

Oxidation of Selected Aromatics Behind Shock Waves

O. Mathieu¹, G. Pengloan², N. Chaumeix and C.-E. Paillard
Institut de Combustion, Aérodynamique, Réactivité et Environnement, CNRS
Orléans, France

¹Currently at: Texas A&M University, College Station, TX, USA.

²Now at: PSA Peugeot-Citroën, La Garenne Colombes, France.

1 Introduction

Aromatic hydrocarbons are important components of gasoline fuels due to their anti-knock properties (related to their high Research Octane Number (RON)) and are consequently found in significant proportion into this kind of fuels: up to 35% vol. in Europe (limited by legislation) and an average of 25% vol. was reported in the US [1]. It is therefore important to characterize and to understand their combustion properties in order to build and validate detailed kinetic models that can help developing internal combustion engine and/or formulating fuels through the use of fuel surrogates [2].

The aim of this study is to provide auto-ignition delay time (τ_{ign}) measurements of aromatic compounds that are present into gasoline fuels, namely toluene (C_7H_8) and ethyl-benzene (C_8H_{10}). To help refining models, τ_{ign} of benzene (C_6H_6) and styrene (C_8H_8) were also investigated. Benzene can be found into gasoline (its amount is however limited by legislation, up to 1% typically, due to its volatility and carcinogenic properties) and is an important combustion intermediate of C_7H_8 [3, 4] and C_8H_{10} [5, 6]. Styrene is an important combustion intermediate of C_8H_{10} [5, 6] and of cyclopentadiene [7], the latest being itself an important combustion intermediate of mono-aromatic species [8].

Ethyl-benzene's autoignition delay has been already studied in shock tube by Shen and Oehlschlaeger [9] but at pressure behind reflected shock waves (P_5) of 10 and 40 atm in air and at equivalence ratio of 0.5 and 1 only. The present study (see Table 1) is therefore an extension of the data set available for this compound. The τ_{ign} of toluene in shock tube was the subject of numerous studies, covering a wide range of conditions [10-13]. The present study complements this large database by slightly extending the range of toluene concentration and pressure investigated. Concerning the benzene, the only study of τ_{ign} in shock tube available in the literature is the study of Burcat et al. [10]. The present work proposes new data at lower benzene concentration and at higher pressure. To our knowledge, there are no shock tube ignition delay measurements for the styrene available into literature.

2 Experimental Setup

Two different shock tubes were used during this study. The first shock tube is composed of a pyrex low pressure section of 9 m long (50 mm i.d.) with a metallic high pressure section of 2 m long. The second shock tube is a stainless steel shock tube of 7.15 m. The high pressure section (114 mm i.d.) is 2 m long while the low pressure section is 5.15 m long (52.5 mm i.d.). The pyrex tube and the

stainless steel tube were used for the low pressure and high pressure studies, respectively. The last section of each tube is equipped with 4 pressure transducers (equally spaced by 150 mm) mounted flush with the inner surface of the tube, the last one being 15 mm before the shock tube end wall. At the same plane as the last pressure transducer, a fused silica window (9 mm optical diameter and 6 mm thickness) is mounted across a UV-sensitive photomultiplier equipped with a narrow-band filter centered on 306 nm which is characteristic of OH emission. The shock wave velocity is deduced from the pressure jump monitored by the pressure transducers. Temperature and pressure behind the incident and reflected shock waves are deduced using the classical procedure [14]. Each shock tube and associated tubing is connected with 2 primary vacuum pumps, which allow for the whole experimental setups to be vacuumed below 1 Pa before every run. The high pressure gas used is He (purity > 99.995%) distributed by AIR LIQUIDE. Hydrocarbons used were > 99.5% purity except for ethyl-benzene (> 99%). Pure hydrocarbons are liquid at ambient temperature so that they had to be vaporized under vacuum conditions. The vapor pressure of the liquid hydrocarbons was maintained below the saturated vapor pressure. The hydrocarbon / oxygen / argon mixtures were prepared in a mixing tank using the partial pressure method. Equivalence ratio (Φ) of 0.5, 1.0 and 1.5 were investigated using very diluted mixtures in order to determine τ_{ign} in conditions where the reactivity of the mixture is not affected by thermal runaway (i.e. τ_{ign} remains controlled by the kinetics only). The experimental conditions, obtained behind reflected shock waves, are summarized in table 1.

Table 1: Experimental conditions

Type	[Fuel] (mol.cm ⁻³)	[O ₂] (mol.cm ⁻³)	[Ar] (mol.cm ⁻³)	T ₅ (K)	P ₅ (MPa)
C ₆ H ₆	5x10 ⁻⁹ – 7x10 ⁻⁷	7x10 ⁻⁸ – 5x10 ⁻⁶	8x10 ⁻⁶ – 1.4x10 ⁻⁴	1300-2000	0.1–2.1
C ₇ H ₈	4x10 ⁻⁹ – 8x10 ⁻⁸	7x10 ⁻⁸ – 8x10 ⁻⁷	8x10 ⁻⁶ – 1.1x10 ⁻⁵	1400-2000	0.145±0.035
C ₈ H ₈	4x10 ⁻⁹ – 10 ⁻⁷	8x10 ⁻⁸ – 8x10 ⁻⁷	9x10 ⁻⁶ – 1.2x10 ⁻⁵	1300-2000	0.145±0.045
C ₈ H ₁₀	3x10 ⁻⁹ – 1.4x10 ⁻⁸	8x10 ⁻⁸ – 10 ⁻⁷	8x10 ⁻⁶ – 10 ⁻⁵	1400-2000	0.14±0.04

3 Experimental Results

This study focuses on the τ_{ign} measurements for various aromatic compounds. The τ_{ign} is defined as the time interval between the moment at which the gas mixture is heated up to the reflected temperature, T₅, and the moment corresponding to 50% of the maximum intensity of the OH emission signal at 306 nm. Auto-ignition delay times vary exponentially with the inverse of the temperature for a given mixture composition and can be formulated with the following Arrhenius relationship [15]:

$$\tau_{\text{ign}} = A[\text{HC}]^a \cdot [\text{O}_2]^b \cdot [\text{Ar}]^c \cdot \exp\left(\frac{+E_a}{R \cdot T}\right)$$

[X]: concentration of the species X in mol.cm⁻³; T: temperature in K; a, b, c: exponents relative to the given species; A: the pre-exponential factor and E_a the activation energy in J.

In a relatively narrow domain of pressure and temperature, these coefficients are generally constant and allow to characterize the behavior of τ_{ign} when the composition is varied.

Toluene / Oxygen / Argon Mixtures

The auto ignition delay times of toluene was studied around the atmospheric pressure for 11 mixtures. Figure 1 presents the results obtained for 9 of these mixtures where toluene (a), oxygen (b) and argon (c) concentrations were kept constant, respectively. As can be seen on Fig.1(a), τ_{ign} decreases noticeably when oxygen is added to the mixture. The effect of the toluene concentration depends on the temperature domain (Fig.1(b)). For the lowest temperatures investigated, the increase in toluene concentration does not affect τ_{ign} , while toluene inhibits its own oxidation on the high temperature side. Fig.1(c) shows that the activation energy is changing considerably at $\Phi = 1$ compared to the other condition investigated (E_a = 269, 236 and 281.5 kJ at $\Phi = 0.5, 1$ and 1.5, respectively). The following expression for τ_{ign} was derived from these results using the classical multiple regression method:

$$\tau_{\text{ign}}(s) = 2.21 \cdot 10^{-13} [C_7H_8]^{0.72} \cdot [O_2]^{-1.1} \cdot \exp\left(\frac{28020}{T}\right)$$

The coefficient over the argon was set to 0 since the pressure was not varied sufficiently during our experiments. The coefficient over the toluene confirms that an increase in the toluene concentration induces an increase of τ_{ign} while the negative coefficient over the oxygen shows the opposite.

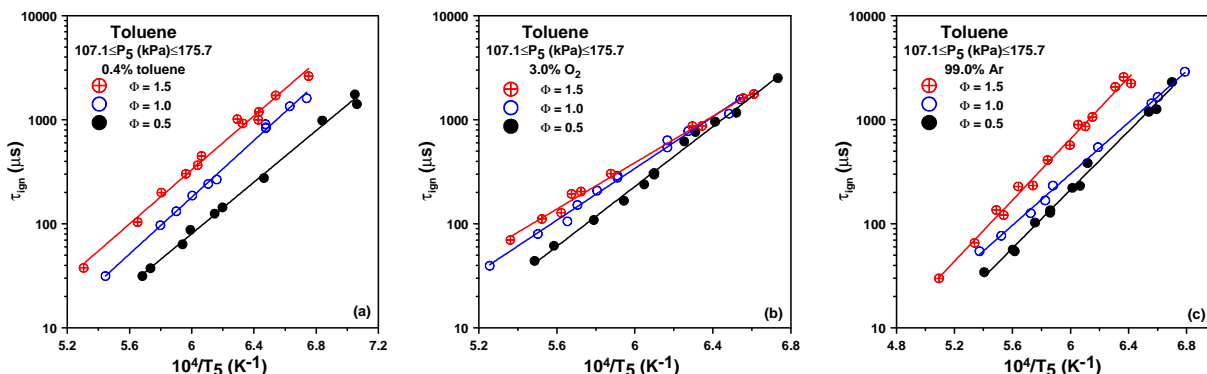


Figure 1: Evolution of the auto-ignition delay times versus $1/T_5$ for toluene (C_7H_8) at $\Phi = 0.5, 1.0$ and 1.5 and at fixed fuel (a), O_2 (b) and Ar (c) concentrations.

Ethyl-benzene / Oxygen / Argon Mixtures

The oxidation of ethyl-benzene was studied for highly diluted mixtures in Ar and results are visible in Figure 2. It can be observed from this figure that the τ_{ign} decreases noticeably with Φ : at 1650 K, $\tau_{\text{ign}} = 460, 330$ and $155 \mu s$ for $\Phi = 1.5, 1.0$ and 0.5 , respectively. At $\Phi = 1$ and above, the activation energy seems to be constant around 270 kJ ($E_a = 273$ and 270 kJ at $\Phi = 1$ and 1.5 , respectively, and $E_a = 245$ kJ at $\Phi = 0.5$).

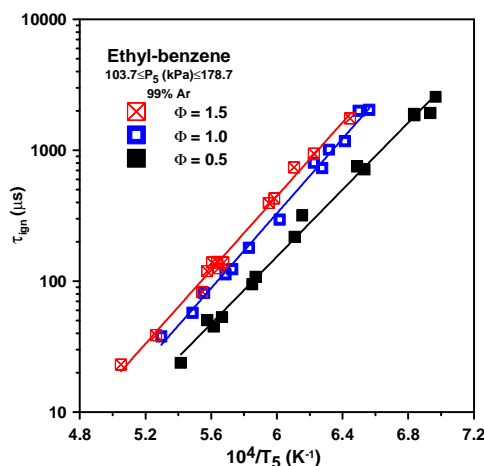


Figure 2: Evolution of the auto-ignition delay times versus $1/T_5$ for ethyl-benzene (C_8H_{10}) at different equivalence ratio and at fixed Ar concentration.

Due to the limited number of experiments performed in this study and due to the fact that results from Shen et al. [9] have been obtained in different conditions (in “air” for Shen et al. [9] and in argon for this study), it was not possible to derive an expression for the auto-ignition delay time of ethyl-benzene.

Benzene / Oxygen / Argon Mixtures

The auto-ignition delay times of Benzene/ O_2 /Ar mixtures were measured behind reflected shock waves for a wide range of benzene concentrations, temperatures and pressures (table 1). Figure 3 presents the results that were obtained at the stoichiometry for a fixed concentration of benzene behind reflected

shock waves ($1.05 \pm 0.2 \times 10^{-7} \text{ mol.cm}^{-3}$) and between $0.15 \pm 0.03 \text{ MPa}$ and $1.8 \pm 0.3 \text{ MPa}$. It is visible that the auto-ignition delay time decreases with the increase in P_5 . This decrease is noticeable between 0.1 and 1 MPa and it seems that a further increase in pressure, from 1 to 1.8 MPa in this study, has a small effect on the variation of τ_{ign} .

The effect of the equivalence ratio on τ_{ign} is visible in Figure 4, where the concentration of oxygen was varied around a fixed concentration of fuel. It can be seen that τ_{ign} decreases notably with Φ in this case. Using results of this study, expressions were derived for τ_{ign} ; one for the low pressure domain (127 experiments) and the second for the high pressure one (50 experiments); and 6 different fuel concentrations were used for each pressure range:

$$\tau_{\text{ign}}(s) = 1.84 \cdot 10^{-14} [C_6H_6]^{0.32} \cdot [O_2]^{-0.98} \cdot \exp\left(\frac{22456}{T}\right) \text{ when } P = 0.14 \pm 0.4 \text{ MPa}$$

$$\tau_{\text{ign}}(s) = 1.22 \cdot 10^{-11} [C_6H_6]^{0.73} \cdot [O_2]^{-1.00} \cdot \exp\left(\frac{21217}{T}\right) \text{ when } 0.4 \leq P(\text{MPa}) \leq 2.07$$

These expressions show that the reactivity of the mixture is increased (τ_{ign} decreases) as O_2 is added to the mixture. The effect of oxygen is similar for the two pressure ranges investigated since the exponent factor on O_2 is similar for the low and high pressure domains. The benzene is exhibiting an opposite trend as a decrease of the mixture reactivity was observed when benzene concentration was increased. This decrease of the reactivity is however more important as the pressure rises (the exponent factor varies from 0.33 at low pressure to 0.73 at high pressure). It was also possible to derive an expression for τ_{ign} that considers all the conditions investigated and all the mixture components. In such case, however, the pressure dependence on the effect of the benzene concentration is not visible:

$$\tau_{\text{ind}}\left(\frac{\text{ms}}{\text{mm}}\right) = 1.48 \cdot 10^{-8} \cdot [C_6H_6]^{0.358} \cdot [O_2]^{-0.939} \cdot [Ar]^{-0.164} \cdot \exp\left(-\frac{21744}{T(K)}\right)$$

Note that the exponent factor on Ar is probably not significant as the variation in the diluent concentration was not important in this study (from 92.8 to 99% mole).

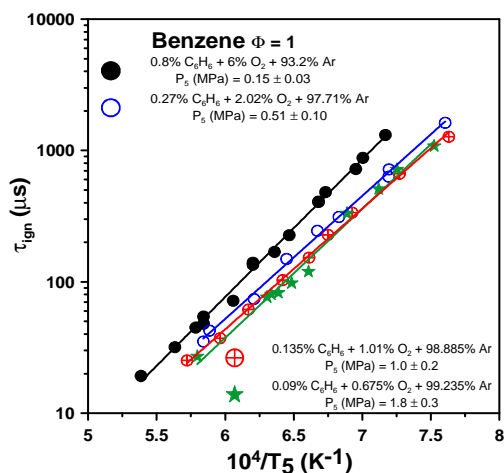


Figure 3: Evolution of τ_{ign} versus $1/T_5$ for the benzene at different pressures behind the reflected shock waves. Benzene concentration fixed at $1.05 \pm 0.2 \times 10^{-7} \text{ mol.cm}^{-3}$.

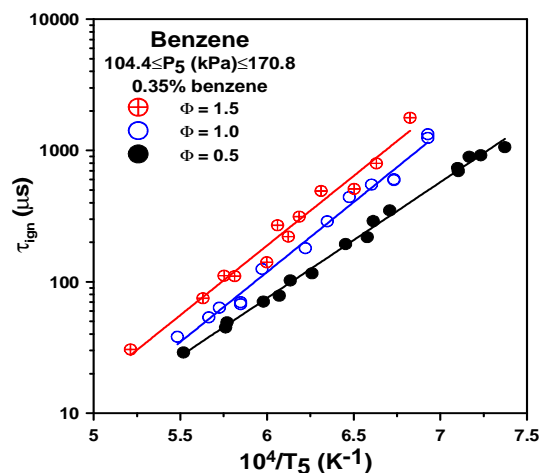


Figure 4: Evolution of the auto-ignition delay times versus $1/T_5$ for benzene at different equivalence ratio and at fixed benzene concentration.

Styrene / Oxygen / Argon Mixtures

Auto-ignition delay times behind reflected shock waves for styrene were measured for 9 different mixtures. Figure 5 presents the results obtained with these 9 mixtures and sorts the results by comparing τ_{ign} at $\Phi = 0.5, 1.0$ and 1.5 for fixed C_8H_8 (a), Ar (b) and O_2 (c) concentrations, respectively.

As reported for the other compounds investigated in this study, τ_{ign} decreases with Φ . The importance of this decrease is however less important when the styrene concentration is varied around a fixed O_2 concentration (Fig. 5 (c)). The following correlation was established for styrene during this study:

$$\tau_{\text{ign}}(s) = 4.27 \cdot 10^{-14} [C_8H_8]^{0.84} \cdot [O_2]^{-1.49} \cdot \exp\left(\frac{23640}{T}\right)$$

Note that the coefficient over the Ar was set to 0 since experiments were performed around the atmospheric pressure only. Coefficients over the styrene and the oxygen concentrations confirm the observations made with benzene, toluene and ethyl-benzene: the reactivity increases as oxygen is added whereas an increase in the fuel concentration induces a decrease of the reactivity.

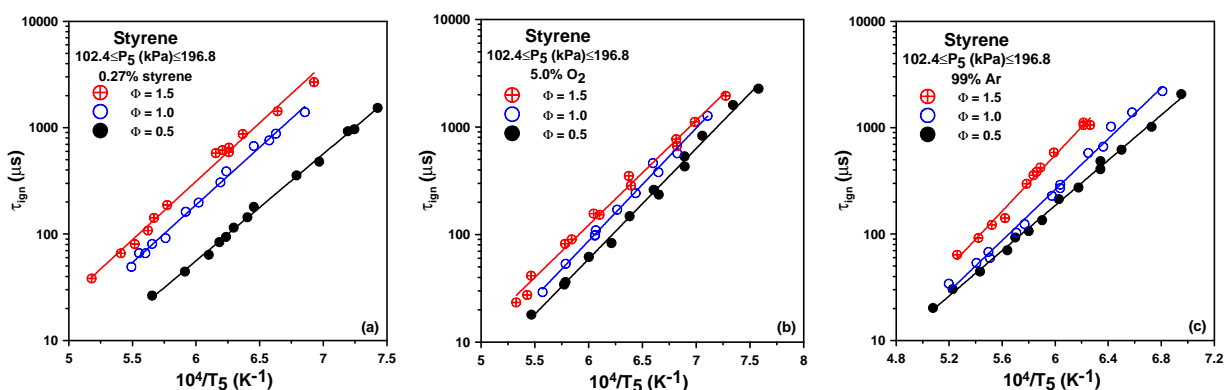


Figure 5: Evolution of the auto-ignition delay times versus $1/T_5$ for styrene (C_8H_8) at $\Phi = 0.5, 1.0$ and 1.5 and at fixed fuel (a), O_2 (b) and Ar (c) concentrations.

Comparison of the results for the different aromatics investigated

Auto-ignition delay times of benzene, toluene, styrene and ethyl-benzene at $P_5 = 141 \pm 38$ kPa for mixtures diluted in 99% Ar are compared in Figure 6 at $\Phi = 0.5$ (a), 1.0 (b) and 1.5 (c). As can be seen in Fig. 6, the effect of oxygen is different from one compound to the other (reduction of τ_{ign} more or less important, different variation in E_a with the equivalence ratio). As a result, it is difficult to rank these aromatics between them. One can however notice that the activation energy of the benzene is consistently lower than for the other fuels. Except at $\Phi = 1.0$, τ_{ign} for toluene are longer than for ethyl-benzene but seem to converge towards a similar value at high temperature.

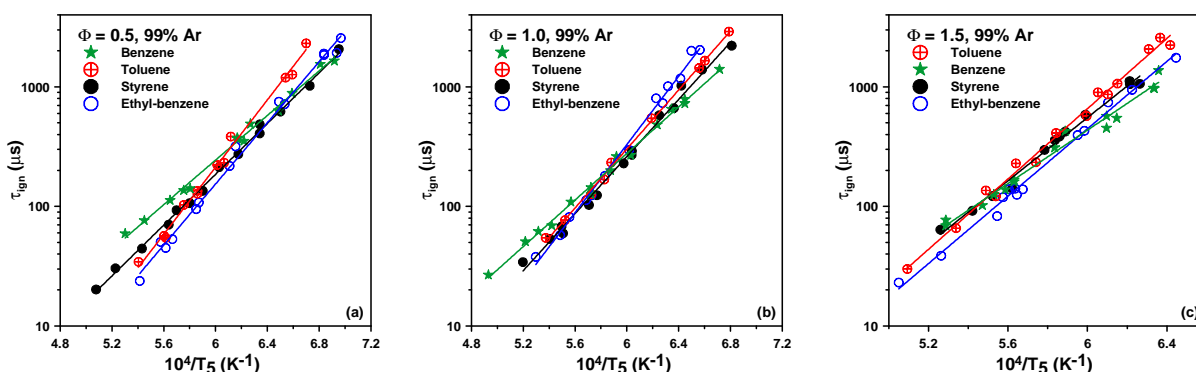


Figure 6: Evolution of the auto-ignition delay times versus $1/T_5$ for benzene, toluene, styrene and ethyl-benzene, $P_5 = 141 \pm 38$ kPa, at $\Phi = 0.5$ (a), 1.0 (b) and 1.5 (c) in 99% Ar mixtures.

4 Conclusion

The study of the auto ignition delay time of aromatic compounds of interest for gasoline fuels, namely benzene, toluene, styrene and ethyl-benzene, has been performed in shock tubes to help validating detailed kinetic models. Most of the experiments were carried out around the atmospheric pressure

although experiments above 1 MPa were performed for benzene. Arrhenius relationships between τ_{ign} and the temperature and the mixture components concentration were derived from experimental results in most of the cases. For each fuel and condition, it was found that the reactivity of the mixture is increased (τ_{ign} decreases) as the oxygen is added to the mixture whereas an increase of the hydrocarbon concentration induces an increase of auto-ignition delay time. Auto-ignition delay times are relatively close between each hydrocarbons under given conditions. The amplitude in the variations of τ_{ign} and in the activation energy can however be different from one fuel to the other. As a result, it is difficult to rank between them the hydrocarbons studied in the conditions investigated.

Acknowledgement

This work was financially supported by Total, PSA, CNRS and ADEME in the framework of ARC-I.

References

- [1] Northrop Grumman, Northrop Grumman Petroleum Product Survey Reports, <http://pps.ms.northropgrumman.com/>.
- [2] M. Mehl et al. (2011). Kinetic modeling of gasoline surrogate components and mixtures under engine conditions. *Proc. Combust. Inst.* 33: 193.
- [3] P. Dagaut et al. (2002). Oxidation, ignition and combustion of toluene: Experimental and detailed chemical kinetic modeling. *Phys. Chem. Chem. Phys.* 4: 1846.
- [4] R. Sivaramakrishnan et al. (2004). High-pressure, high-temperature oxidation of toluene. *Combust. Flame* 139: 340.
- [5] T. A. Litzinger et al. (1986). The oxidation of ethylbenzene near 1060K. *Combust. Flame* 63: 251.
- [6] G. Pengloan (2001). Etude cinétique de l'oxydation de composés aromatiques : Application à la formation de polluants dans les moteurs automobiles. Phd Thesis, Université d'Orléans, France.
- [7] R. G. Butler and I. Glassman (2009). Cyclopentadiene combustion in a plug flow reactor near 1150 K. *Proceed. Combust. Inst.* 32: 395.
- [8] M. Mehl et al. (2009). Chemical kinetic study of the oxidation of toluene and related cyclic compounds. *Proceed. 6th US National Combust. Meeting*, May 17-20, 2009, Ann Arbor, Michigan.
- [9] H.-P. Shen, M. A. Oehlschlaeger (2009). The autoignition of C₈H₁₀ aromatics at moderate temperature and elevated pressures. *Combust. Flame* 156: 1053.
- [10] A. Burcat et al. (1986). Ignition delay times of benzene and toluene with oxygen in argon mixtures. NASA TM-87312.
- [11] V. Vasudevan et al. (2005). Shock tube measurements of toluene ignition times and OH concentration time histories. *Proceed. Combust. Inst.* 30: 1155.
- [12] D. F. Davidson et al. (2005). Shock tube ignition measurements of iso-octane/air and toluene/air at high pressures. *Proceed. Combust. Inst.* 30: 1175.
- [13] Hsi-Ping S. Shen et al. (2009). A shock tube study of the auto-ignition of toluene/air mixtures at high pressures. *Proceed. Combust. Inst.* 32: 165.
- [14] W. C. Jr Gardiner et al. (1981). *Shock Waves in Chemistry*, A. Lifshitz (Ed.), Marcel Dekker, Inc., New York: 319.
- [15] A. Lifshitz et al. (1971). Shock Tube Investigation of Ignition in Methane oxygen-argon Mixtures. *Combust. Flame* 16: 311.