

OVERALL ACTIVATION PARAMETERS OF PROPYLENE OXIDATION IN PREMIXED FLAMES

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abstract: The addition of diluents (Ar, CO₂ or air) to a stoichiometric propylene-air mixture determines an important decrease of average flame front temperature and consequently, a decrease of the average reaction rate within the flame front, as seen from burning velocity of these mixtures. The analysis of burning velocity variation against the total initial pressure and the average flame front temperature enabled the determination of the overall reaction order and overall activation energy, respectively. Such overall activation parameters are important for modelling the flame propagation in various conditions (stagnant or flowing mixtures, laminar or turbulent flow etc)

Introduction

The overall activation parameters of fuel oxidation in flames are important in many engineering applications such as CFD (Computational Fluid Dynamics) modelling of flame propagation in confined and unconfined conditions or in vented explosions [1]. The overall activation parameters (reaction order and activation energy) are readily obtained from the analysis of burning velocity dependency on the total initial pressure of fuel-oxidant mixture and on the average flame front temperature, using the relationships developed within the theory of laminar flame propagation [2,3]. In the present paper, the variation of flame front temperature was obtained by dilution of a stoichiometric fuel-air mixture with several diluents: Ar, CO₂ or air. Propylene was examined since few data on its burning velocity, especially in the presence of inert gases, are available. Burning velocities of propylene-air and propylene-air-inert mixtures (inert concentrations within 5 ÷ 20 vol. %) were determined using pressure-time records from a spherical bomb with central ignition, at ambient initial temperature and total initial pressures within 0.3 - 1.2 bar.

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Experimental procedure and computing program

The explosion vessel was a stainless steel spherical bomb able to withstand pressures of 30 bar. The bomb was fitted with stainless steel electrodes and the spark gap was located in the bomb centre. Electric sparks produced by a standard motorcar induction coil were used for explosion initiation. The pressure variation during flame propagation was continuously monitored by means of a pressure transducer (Kistler 601A, coupled with a Charge Amplifier Kistler 5001 SN) and the flame front position was determined by means of an ionisation gauge. Both signals were recorded and stored by a digital acquisition system Tektronix TestLab 2505, usually at 10^4 signals per s. Other characteristics of the experimental set-up were previously given [4].

The explosive mixtures were obtained by partial pressure method, in 10 L steel cylinders, at 4 bar total pressure. The experiments were performed at ambient temperature and various total initial pressures within 0.3 and 1.2 bar.

Propylene (99.5%) was purchased from Arpechim Petrochemical Plant-Pitesti.

Compressed air, argon (99.99%) and carbon dioxide (99.5%) were purchased from SIAD-Italy. They were used without further purification

The normal burning velocity, S_u , was calculated from pressure-time records of explosion development in a spherical vessel, during the early stage of the process, according to the recently developed procedure [5] based on determination of cubic law coefficients of pressure rise.

The adiabatic flame temperatures of fuel-air and fuel-air-diluent mixtures were computed with the program ECHIMAD [6], assuming that chemical equilibrium is reached within the flame. Fifteen compounds (C_{graphite} , CH_4 , CO , CO_2 , H_2O , H_2 , O_2 , N_2 , NO , C_2H_2 , C_2H_4 , C_3H_8 , H , OH and O) were considered as combustion products. Their heat capacities (expressed as function of temperature with the form: $C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^{-2}$), the standard enthalpies of formation at 298 K and the standard entropies at 298 K were taken from the collections of Stull [7], Barin [8] and Kubaschewki [9].

Results and Discussion

A set of data referring to propylene-air-argon mixtures with various argon concentrations is given in Figure 1. For each mixture, the burning velocity decreases as the total initial pressure, p , increases. Indeed, according to the theory of laminar flame propagation, the dependency of burning velocity of fuel-oxidant mixtures on mixture pressure p has the form:

$$S_u = S_u^{ref} \left(\frac{p}{p_{ref}} \right)^\beta \quad (1)$$

where β is the baric coefficient (pressure exponent) of the burning velocity, p_{ref} is the reference pressure (usually, the ambient pressure) and S_u^{ref} is the burning velocity evaluated in reference conditions. For all hydrocarbon-air mixtures, negative values of baric coefficients are reported [3].

The overall reaction orders, n , are calculated from the baric coefficients according to the equation [10]:

$$n = 2(\beta + 1) \quad (2)$$

Data referring to propylene-air-diluent mixtures are given in Table 1. The baric coefficients were calculated as slopes of the linear correlations $\ln S_u$ versus $\ln p$.

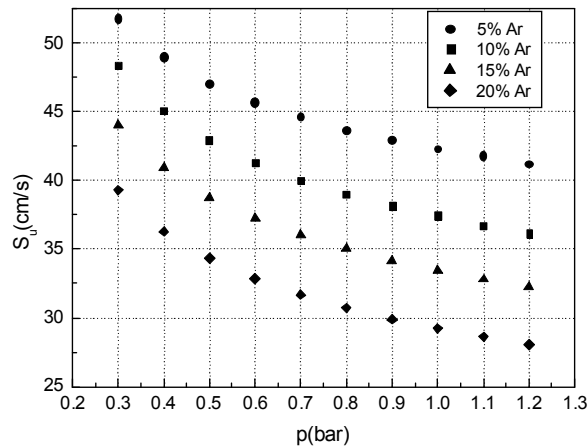


Fig. 1: The influence of Ar dilution on burning velocity, for a stoichiometric propylene-air mixture

Table 1. Pressure exponents of burning velocities in propylene-air-argon and propylene-air-carbon dioxide mixtures, β , and overall reaction orders n of propylene oxidation.

No.	[C ₃ H ₆] (vol%)	[diluent] (vol%)	Argon		Carbon dioxide	
			$-\beta$	n	$-\beta$	n
1	4.46	0	0.160	1.68	0.160	1.68
2	4.28	5.0	0.161	1.68	0.191	1.62
3	4.05	10.0	0.208	1.58	0.231	1.54
4	3.83	15.0	0.222	1.56	0.257	1.49
5	3.60	20.0	0.240	1.52	0.193	1.62

Similar data referring to propylene-air mixtures are given in Table 2.

Table 2. Pressure exponents of burning velocities in propylene-air mixtures, β , and overall reaction orders of propylene oxidation, n .

[C ₃ H ₆] (vol%)	3.22	3.47	3.76	4.11	4.46	4.78	5.03
$-\beta$	0.28	0.19	0.19	0.21	0.16	0.20	0.18
n	1.44	1.62	1.62	1.57	1.67	1.60	1.65

Excepting the leanest mixture ([C₃H₆] = 3.22%), all propylene-air mixtures have the same overall reaction order $n = 1.60$, within experimental errors. Close values of the overall reaction orders, $n = 1.80 - 2.0$, were calculated from the pressure dependence of quenching distances [11]. For propylene-air-diluent mixtures, the overall reaction orders have also values between 1.80 and 1.50, decreasing with the increase of diluent concentration.

The overall activation energy of fuel-oxygen reaction within the flame front was calculated with the equation [12]:

$$\ln S_u + \frac{1}{2} \ln T_{fl,av} - \frac{n}{2} \ln Y = const - \frac{E_a}{2RT_{fl,av}} \quad (3)$$

where $T_{fl,av}$ is the average adiabatic flame temperature within the flame front and Y is the mole fraction of reactive components (fuel + oxidant) in the examined mixture. The average temperature is calculated with the relationship [12]:

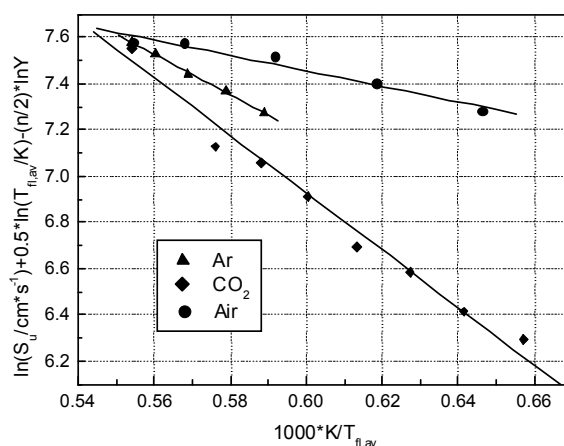
$$T_{fl,av} = T_0 + 0.74(T_{fl} - T_0) \quad (4)$$

A typical set of data is given in Table 3; an average value of reaction order ($n = 1.60$) was used. For propylene-air-carbon dioxide mixtures, we used $n = 1.74$.

Fig. 2 shows the plots of the left member of eqn. (3) against the reciprocal value of average flame temperature, for a stoichiometric propylene-air mixture diluted with Ar and with CO₂. In Fig. 2, data referring to lean propylene-air mixtures (using $n = 1.60$) were also plotted. One may consider that such mixtures were obtained by adding excess air to the stoichiometric propylene-air system. The slopes of linear correlations give the overall activation energies.

Table 3. Burning velocities and flame temperatures of propylene-air-argon mixtures, at $p_0 = 1$ bar and $T_0 = 298$ K

[C ₃ H ₆] (vol%)	[Ar] (vol%)	T_{fl} (K)	$T_{fl,av}$ (K)	Y	S_u (cm/s)	$\ln(\frac{S_u}{cm \cdot s^{-1}}) + \frac{1}{2} \ln(\frac{T_{fl,av}}{K}) - \frac{n}{2} \ln Y$	$\frac{1000 \cdot K}{T_{fl,av}}$
4.46	0.0	2335.2	1804.7	1.00	46.04	7.57859	0.55411
4.28	5.0	2308.2	1784.8	0.95	42.22	7.52746	0.56029
4.05	10.0	2271.8	1757.8	0.90	37.32	7.43973	0.56889
3.82	15.0	2230.7	1727.4	0.85	33.42	7.36635	0.57891
3.60	20.0	2191.1	1698.1	0.80	29.22	7.27200	0.58889


Fig. 2: The dilution effect of Ar, CO₂ and air on burning velocity, for stoichiometric propylene-air-diluent mixtures; data evaluated at $p_0 = 1$ bar and $T_0 = 298$ K

The results are given in Table 4.

Table 4 – Overall activation energies of propylene oxidation in flames, E_a (kJ/mol)

	Ar	CO ₂	Excess air
Propylene-air-diluent	146	207	56

Such values can be obtained also for any initial pressure within the studied range (0.3 – 1.2 bar), using adequate values of average flame temperature. Earlier values of the overall activation energy, determined by means of preheating method, for propylene-air mixtures with various propylene concentrations are higher: 165 kJ/mol for a lean mixture ([C₃H₆] = 3.51%) and 177 kJ/mol for the stoichiometric mixture ([C₃H₆] = 4.52%)

A similar analysis of earlier reported burning velocities of stoichiometric propylene-oxygen-nitrogen mixtures ([N₂] = 45 – 75 %)[13] gave $E_a = 161$ kJ/mol. The result is in good agreement with $E_a = 176$ kJ/mol determined from burning velocity measurements of

C₃H₆- O₂- N₂ flames stabilised on a burner, at ambient pressure [12] and with E_a = 160 - 176 kJ/mol determined from induction delays of propylene-oxygen self-ignition [14].

The dilution by Ar or CO₂ of the stoichiometric propylene-air mixture has little influence on the overall reaction order, which varies within 1.50 and 1.70. The dilution effect is observed in values of the overall activation energy: 146 kJ/mol (C₃H₆-air-Ar) and 207 kJ/mol (C₃H₆-air-CO₂) as compared to 56 kJ/mol at dilution by air. These values are relevant for the significant inerting effect of carbon dioxide on flame propagation in fuel-air mixtures.

4. Conclusions

The rate of fuel-oxidant reaction within the flame front can be described by means of overall activation parameters: overall reaction order and overall activation energy. These parameters were determined for a test fuel-oxidant system: propylene-air, in the presence of excess air or Ar and CO₂ as diluents, from burning velocities in systems at various initial pressures and various diluent concentration.

The overall reaction order has values between 1.50 and 1.80, for all investigated systems, as reported for many other hydrocarbon-air mixtures. The overall activation energies have also typical values for oxidation of hydrocarbons in flames.

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