

# ACTIVATION ENERGY VARIATION DURING IGNITION OF PROPANE-AIR MIXTURES ON ISOTHERMALLY HEATED PLATINUM FILAMENTS

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**abstract:** The ignition of a stagnant stoichiometric propane-air mixture by an isothermally heated platinum filament supported on a thin quartz bar was studied at various filament temperatures between 400 and 600 K and at ambient pressure. The heterogeneous ignition over the platinum surface continues in the gaseous phase as an independent flame. The induction periods of the gas-phase ignition at various filament temperatures were used to evaluate the overall activation energy of the process. The chemical heat flux variation during surface reaction exhibits an anti Arrhenius behaviour and allows an evaluation of a continuous change of the apparent activation energy.

## 1. Introduction

The ignition of gaseous flammable mixtures on hot solid surfaces is a frequent phenomenon having numerous implications and applications in a variety of combustion problems [1÷3]. Special aspects connected with this subject arise from the catalytic effect of solid surfaces [4÷5]. Particularly, the catalytic oxidation of hydrocarbons on platinum has received wide attention in recent years due to the use of platinum as one of the active components in automotive exhaust catalytic converters. The experimental information and theoretical analysis of the ignition indicate the existence of some critical conditions necessary for its occurrence. A very specific property characterizing the system is the induction period of the ignition and its dependence on the mixture pressure and composition as well as on the surface temperature [5÷7]. The variation of this property on the system variables gives valuable information on the kinetics of process. The simple models which give the pressure and composition dependence of the induction period refer to initial gas composition, before the ignition. Depending on the relative value of the induction period as well as on the relative contribution of chemical reactions and transport processes, this composition can be significantly changed. The aim of the present paper is to report the measured induction periods of a stoichiometric propane-air mixture for gas-phase ignition on a heated platinum filament at various filament temperatures and to calculate the overall activation energy and its variation during this transient period. The ignition source, serving also as a detector of

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the processes accompanied by heat exchange, ensures a quasi-rectangular temperature jump, followed by an isothermal heating. The fast response of the platinum filament with respect to heat exchange processes is expected to give detailed information on the local changes. The stoichiometric propane – air mixture was thoroughly examined in many laboratories and there are reliable reference data in literature for comparison [4,8,9].

## 2. Experimental apparatus and procedure

The experimental equipment contains four major parts: (1) the gas feed and evacuation with gas control and monitoring system, (2) the explosion cell equipped with a platinum filament as ignition source, (3) the power supply and (4) the data acquisition system.

A specially designed electrical circuit is used to produce a quasi-rectangular jump of the wire temperature and to keep it constant. A platinum wire coiled as filament with resistance  $R_f$ , a standard resistor with resistance  $R_{st}$  and a potentiometer form a Wheatstone bridge. The discharge of a condenser previously charged at a suitable voltage (established by trial and error) across the filament in less than 1 ms insures the temperature jump, while an integrated circuit senses the bridge unbalance and adjusts the feed voltage through a transistor, permitting a continuous monitoring of  $R_f$ . The initial setting of potentiometer adjusts the value of  $R_f$  and consequently the filament temperature [10,11]. The transient or stationary voltages across  $R_{st}$  are recorded using a data acquisition system Tektronix-TestLab 2505, provided with a 4-channel acquisition card type 25AA1.

To maintain the symmetry of the platinum filament, it was supported on a thin quartz bar ( $\phi = 1$  mm,  $l = 50$  mm). Experiments were made at various filament temperatures (within the range 437÷589 K), at a constant pressure (100 kPa) and stoichiometric composition (4.02 vol.% propane) of propane-air mixture. The platinum filament temperature was calculated from the circuit characteristics using the following equation taken from literature:

$$\rho = A + Bx + Cx^2 \quad (1)$$

where  $\rho = R_f/R_f^0$  is the relative resistance,  $R_f^0$  is the filament resistance at 0°C,  $x$  is the temperature (in °C) and  $A, B, C$  are constants ( $A = 1, B = 3.97427 \cdot 10^{-3}, C = 5.844 \cdot 10^{-7}$  [12]).

## 3. Results and Discussion

The ignition on catalytically active surfaces is a complex process implying as a first step the ignition of the surface reaction, occurring even outside the flammability limits of fuel, followed subsequently by the gas phase ignition occurring within the explosivity range. There is a strong interaction between surface and gas phase ignition [13÷17]. While for noncatalytic surfaces the combustion reaction is initiated within a thin layer of gas surrounding the solid surface, for catalytic surfaces the process starts as a surface reaction implying adsorbed species. When the critical conditions are attained, the gas phase reaction propagates into the whole mixture. Since the combustion reactions in the adsorbed layer or in the adjacent gas phase are exothermal, their occurrence can be easily identified on the

experimental curve giving the voltage across the standard resistor in time. The output of the acquisition system for a typical run with the platinum filament on a quartz bar in air or in the test mixture is given in Fig. 1 as voltage across the standard resistor,  $U_{st}$  in time. It can be easily seen that the exothermic reactions can be identified as a lowering of the input voltage necessary to maintain a constant temperature. The initial decreasing represents the surface reaction, while the sudden decrease represents the ignition of the gas reaction.

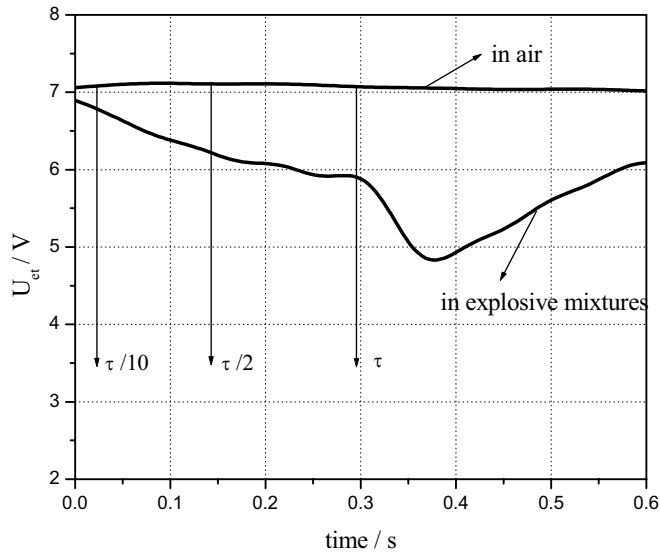


Fig. 1: Output of the acquisition system for a typical run: voltage across the standard resistor,  $U_{st}$  with the platinum filament on a quartz bar in air or in the test mixture  
The data refer to a stoichiometric  $C_3H_8$ -air mixture at  $p_0 = 100$  kPa and  $T_f = 1040$  K.

On  $U_{st} = f(t)$  diagrams, the induction period can be measured as a function of the initial pressure,  $p_0$ , and the filament temperature,  $T_f$ . The thermal ignition theory indicates that the induction period,  $\tau_i$ , can be expressed as a function of  $p_0$  and  $T_f$  by the relationship [1,17]:

$$\tau_i = a \cdot p_0^{-n} \cdot e^{\frac{E_a}{RT_f}} \quad (2)$$

where  $n$  is the overall reaction order,  $E_a$  is the activation energy, and  $R$  is the gas constant.

At constant pressure (100kPa) the following results were obtained from the plot  $\ln \tau = f(1/T)$  (Fig. 2): the slope =  $(9.06 \pm 1.36) \times 10^3$ , the intercept =  $-3.03 \pm 1.26$  with the correlation coefficient 0.968. The corresponding activation energy of the gas phase ignition process is  $E_a = 75.3$  kJ.mol<sup>-1</sup> which can be compared with the reported data of Hiam, Wise and Chaikin [4], who obtained  $E_a = 114$  kJ.mol<sup>-1</sup> and with the result from Vesper and Schmidt [8,9], who obtained  $E_a = 80$  kJ.mol<sup>-1</sup>, for the surface ignition of propane-air stoichiometric mixtures on platinum. Because of the relatively high values of the induction periods (up to 0.3 s) one can suppose that there is a significant change of mixture composition within the

reaction layer due to chemical reaction, so that the kinetics of the surface reaction might be dependent on the variable local composition of mixture in time. It is also possible for the surface combustion to change its mechanism between its start and the ignition of gas phase reaction. All these processes are likely to induce a change of the overall activation parameters. In order to check this possibility, we examined the heat flux (which is correlated with the reaction rate) for different fractions of the induction period, for each surface temperature. It is assumed that the induction period is a characteristic property of the system and its fractions characterize also the process evolution in the same way for each surface temperature. An examination of the heat flux for a specific fraction at different temperatures would give a corresponding apparent activation energy.

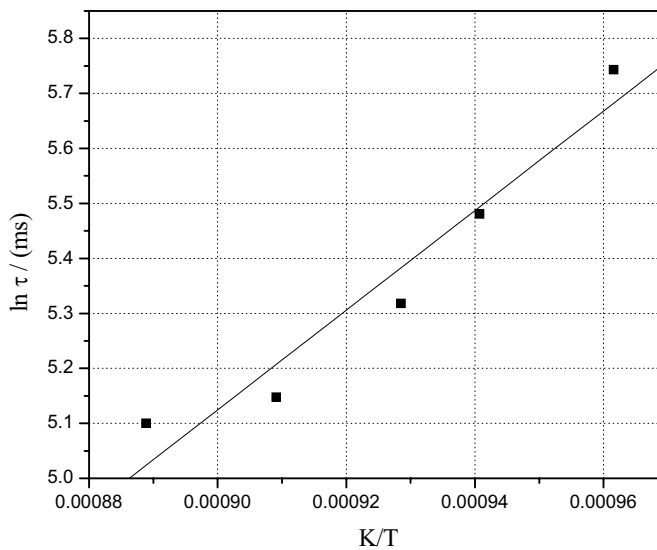


Fig. 2: Induction periods of ignition for a stoichiometric  $C_3H_8$ -air mixture at  $p_0 = 100$  kPa by a platinum filament supported on a quartz bar, at various temperatures

The difference between the rates of heat transfer from the filament to air and to an explosive mixture originates essentially in the exothermic combustion reaction. The rate of the chemical heat release  $dQ_r/dt$  can be considered equal to this difference and calculated as [10]:

$$dQ_r/dt = \frac{R_f}{R_{st}^2} \left[ (U_{st}^2)_{air} - (U_{st}^2)_{mixture} \right] \quad (3)$$

To visualize the variation of the activation energy during the transient period, the heat fluxes for different fractions of the induction period ( $\tau/z$ , where  $1 < z < 10$ ) were calculated.

If  $dQ_r/dt$  is related to the rate of the overall combustion reaction, the following relationship is obtained:

$$\left(\frac{dQ_r}{dt}\right) = \alpha \cdot p_0^n \cdot (X_{\text{ox}}^{n_1} \cdot X_f^{n_2}) \cdot e^{-\frac{E_a}{RT_r}} \quad (4)$$

where, as a first approximation,  $\alpha$  is a constant,  $X_{\text{ox}}$  and  $X_f$  are the molar fractions of oxygen and fuel, respectively, and  $n_1$ ,  $n_2$  are the corresponding reaction orders. This relationship can be used at the end of the ignition period, as well as for its different fractions and can be also extrapolated to initial conditions, when the mixture composition within the reaction layer is known. An illustrating plot at the end of induction period is given in Fig. 3 as  $\ln(dQ_r/dt)$  against  $1/T$ . The correlation between the reaction heat flux and the surface temperature is very good for such processes where there are many uncontrolled factors. Similar analyses were made for different induction period fractions. The results are given in Table 1. A systematic increase of the apparent activation energy from higher to lower fractions can be observed. This variation is given in Fig. 4.

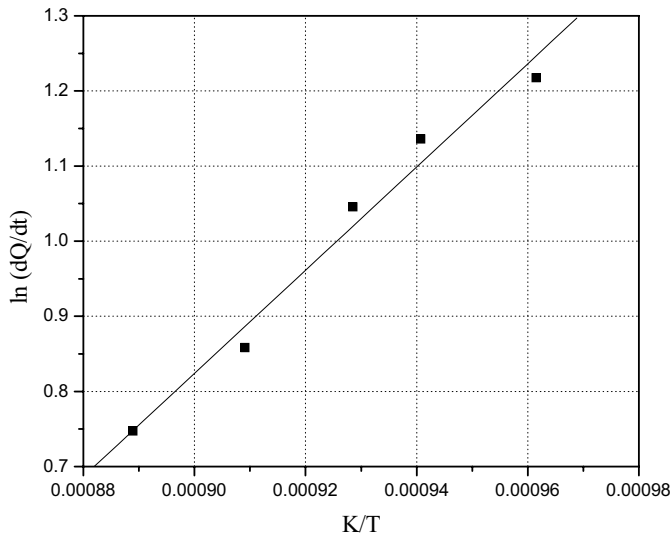


Fig. 3: Rate of heat release at the surface ignition with a Pt filament supported on quartz of a stoichiometric  $C_3H_8$ -air mixture at  $p_0 = 100$  kPa

An examination of the results given in Fig. 3 and 4, as well as those presented in Table 1, indicates an anti Arrhenius dependence of  $\ln(dQ_r/dt)$  with respect to  $1/T$  which, according to equation (4), should give a negative slope. A similar trend was also reported for a 4.47 vol% propylene/air mixture at normal pressure for temperatures between 1000 and 1200K [19], using the same experimental technique. Such behaviour, although unusual, is not quite surprising for a catalytic surface. Numerous experimental observations indicate that the catalytic surfaces require higher ignition temperatures as compared to noncatalytic ones [13÷18], a result which contradicts the expected Arrhenius kinetics. It was shown [18] that there are situations under which an increase in the surface temperature can result in an inhibition of its ignition ability due to extensive reactant depletion within the adjacent gaseous layer, enhanced by the catalytic effect. If the mass transfer is not able to compensate rapidly this reactant deficit, the overall reaction rate can decrease with

temperature increasing. This possibility is explicitly shown in equation (4) through the presence of the oxygen and fuel molar fractions,  $X_{\text{ox}}$  and  $X_{\text{f}}$ . Within restricted experimental conditions, when the mass transfer cannot compensate the reactant depletion, the decrease of the product  $(X_{\text{ox}}^{n_1} \cdot X_{\text{f}}^{n_2})$  can compensate the Arrhenius increase of the overall rate constant. Consequently the reported values of the apparent activation energies represent composite quantities containing both the overall activation energy and the temperature variation of the local composition. In agreement with theoretical predictions [18], such compensations are likely to occur especially for catalytic ignitions in stagnant mixtures.

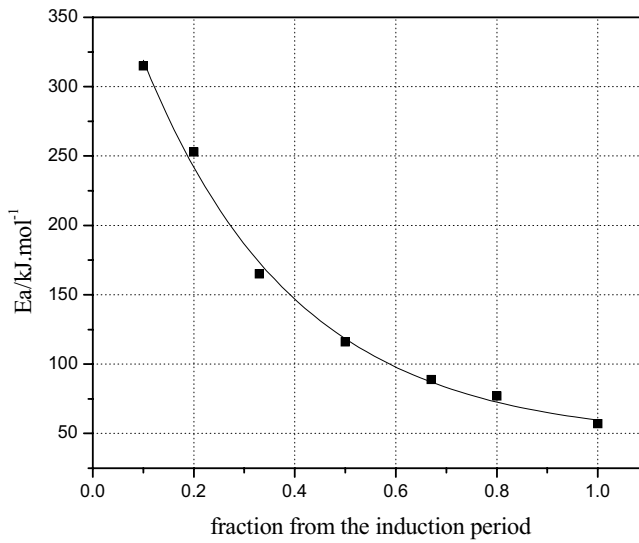


Fig. 4: Variation of the apparent activation energy against the fraction from the induction period, for a stoichiometric  $C_3H_8$ -air mixture at  $p_0 = 100$  kPa

Table 1. Regression parameters of linearized form of equation (4) for different induction period fractions

$\tau/z$	Slope	Intercept	Correlation Coefficient	$E_a/\text{kJ.mol}^{-1}$
$\tau/10$	$(37.9 \pm 12.6)10^3$	$-36.2 \pm 13.5$	0.832	$315 \pm 105$
$\tau/5$	$(30.5 \pm 5.11)10^3$	$-28.6 \pm 4.73$	0.960	$253 \pm 42.5$
$\tau/3$	$(19.9 \pm 3.36)10^3$	$-18.3 \pm 3.11$	0.960	$165 \pm 29.9$
$\tau/2$	$(13.9 \pm 1.74)10^3$	$-12.4 \pm 1.61$	0.977	$116 \pm 14.5$
$\tau/1.5$	$(10.7 \pm 1.52)10^3$	$-9.20 \pm 1.41$	0.971	$88.9 \pm 12.6$
$\tau/1.25$	$(9.27 \pm 1.30)10^3$	$-7.72 \pm 1.20$	0.972	$77.0 \pm 10.8$
$\tau/1$	$(6.87 \pm 0.596)10^3$	$-5.36 \pm 0.552$	0.989	$57.1 \pm 4.95$

For many fuel/air mixtures, where the catalytic ignition occurs in flow systems, such phenomena were not encountered. This can be explained by the renewal of reactant concentrations brought about by convection. It is expected that a partial renewal of

reactants within the reaction zone can be also ensured by the natural convection that supplements the mass transfer provided by the molecular diffusion. The variation of the apparent activation energy within the ignition period indicates a higher effect of reactant depletion at the beginning of the surface reaction, which subsequently decreases due probably to natural convection. An important contribution to the decrease of the convection mechanism, especially during the early stages, is likely to be brought by the presence of the quartz bar used to support the platinum filament in order to maintain its symmetry. It should be noted that small changes in experimental conditions could induce important variations of the mass transport mechanism, explaining the large spread of data obtained in this field.

## Conclusions

The gas-phase ignition of a stoichiometric propane-air mixture was studied using an isothermally heated platinum filament supported on a thin quartz bar at different temperatures and ambient pressure. The induction periods for different filament temperatures were measured and the overall activation energy of the gas-phase ignition was evaluated. The obtained value is close to other reported values for the surface ignition process. From the analysis of the chemical heat flux during the transition from surface to gas-phase ignition, an anti Arrhenius behaviour of the overall chemical reaction, as well as a significant variation of the apparent activation energy for the surface reaction were found. The results were explained assuming an important reactant depletion during the ignition period, in accord with current opinions regarding the effects of catalytic surfaces at high temperatures.

## Acknowledgements

The authors acknowledge the financial support of the Romanian Ministry of Education and Research under Research Grant nr.32/2002.

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