

TRANSITION FROM KINETIC TO DIFFUSION CONTROL DURING THE CATALYTIC IGNITION OF ALKANE/AIR MIXTURES ON PLATINUM

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The catalytic ignition of stagnant stoichiometric propane or butanes/air mixtures on isothermally heated platinum wires, using a quasi-rectangular temperature profile, is characterized by two distinct stages: a transient one when the reaction rate increases from zero to a limiting value, followed by quasi steady-state combustion, limited by the reactant diffusion toward the catalyst surface. The steady state combustion is reached after a characteristic period τ_s . The experimental technique allows the measurement of the reaction heat flow rate during both regimes at temperatures significantly higher than the catalytic ignition temperatures. The analysis of the transient period offers the possibility to evaluate the variation of the activation energy during this period, using the measured reaction heat flow rates at various temperatures and different fractions of τ_s .

INTRODUCTION

The catalytic ignition of fuel/air mixtures, a very important step in catalytic combustion, is considered to be a sudden transition from kinetic to diffusion control.^{1,2} The overall process occurs at characteristic temperatures and is dependent on the composition, fuel type and total pressure as well as on the catalyst nature and state. The measurement of the critical ignition temperatures, using different experimental techniques, allows the determination of the kinetic parameters, according to specific

models for the overall ignition process³⁻⁸ or for some of its steps.^{9,10}

The ignition temperature is customarily determined in a stream of combustible mixture, when the catalyst temperature is increased slowly until the combustion rate increases suddenly. The increase of the heterogeneous catalytic reaction rate with catalyst temperature is illustrated qualitatively in Fig. 1.¹¹ It is obvious that the transition is not of the step type and this can partially explain the diversity of the reported results obtained using various techniques.

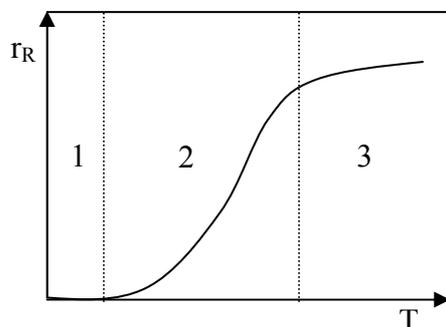


Fig. 1 – Surface reaction rate, vs temperature, for a heterogeneous catalytic combustion: 1. kinetic control; 2. transition from kinetic to mass transfer control; 3. mass transfer control.

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Besides, the change in the slope of the reaction rate with temperature indicates the existence of high activation energy at lower temperatures followed by a continuous decrease after the inflexion point.

A recently reported procedure¹², based on the catalytic ignition in stagnant combustible mixtures using a quasi-rectangular temperature profile of a platinum wire, offers a detailed analysis of the transition from the kinetic to the mass transfer (diffusion) control. It is based on the measurement of the reaction heat flow rate during the ignition process on isothermally heated platinum wires. The reaction heat flow rate is directly connected to the catalytic reaction rate and can be measured during both transient period of ignition and steady-state catalytic combustion.

The present paper aims to present the analysis of the transient ignition period for stoichiometric mixtures of propane, *n*-butane and *i*-butane with air at temperatures significantly higher than the catalytic ignition temperatures. The catalytic combustion of these alkanes was less studied, although they are the main components of the liquefied petroleum gas, a composite fuel involved in many practical applications. The temperature dependence of the reaction heat flow rate during the transient ignition period reveals the continuous change of the overall activation energy.

EXPERIMENTAL METHOD

The details regarding the experimental set up referring to the reaction heat flow rate measurements on isothermally

heated platinum wires and to the sample preparation were given elsewhere.^{12,13} Samples of air or fuel/air mixture are sequentially introduced into the evacuated test cell at the same initial pressure and a platinum wire, located in the centre of the cell, is heated following a quasi-rectangular profile and is subsequently maintained at a constant temperature. The wire is connected in series with a standard resistor which allows the monitoring of the input power on the wire during the isothermal heating.

The reaction heat flow rate dQ_r/dt can be calculated as:

$$dQ_r/dt = (R_w/R_{std}^2) \cdot [(U_{std}^2)_{air} - (U_{std}^2)_{mixture}] \quad (1)$$

where Q_r is the heat delivered by the exothermal catalytic reaction, R_w and R_{std} are the wire and standard resistances and U_{std} is the voltage across the standard resistor in air or in mixture, respectively. All involved quantities are experimentally measurable. The necessary gas pressure and wire temperature are measured according to described procedures.

The plot of dQ_r/dt versus time indicates the existence of a transient period, where dQ_r/dt increases from a small value, resulted from the fast combustion of the adsorbed components on the platinum wire at initial (ambient) temperature, up to a limiting constant value, characteristic to a steady-state regime, controlled by reactant diffusion toward the platinum wire.¹² As long as the bulk concentrations of the components remain approximately constant, this limiting value remains also constant but it decreases steadily for longer times due to the continuous consumption of reactants in the test cell. The analysis of the steady-state regime allows the evaluation of the kinetic parameters from measurements at various compositions, pressures and temperatures. Likewise, the transient period contains valuable information on changes occurring between the beginnings of the heterogeneous combustion and the attainment of the steady-state.

A typical plot of dQ_r/dt vs time during the transient period is given in Fig. 2.

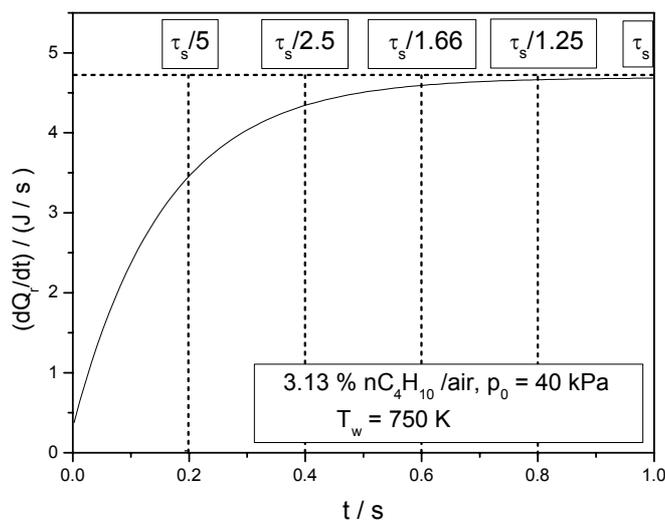


Fig. 2 – The reaction heat flow rate increases during the transition period; τ_s is the time required to attain the steady-state catalytic combustion. dQ_r/dt can be evaluated at different fractions of τ_s .

THE KINETIC MODEL

The diagram presented in Fig. 2 is adequately described by an equation of the form:

$$\frac{dQ_r}{dt} = a + b \cdot (1 - \exp(-ct)) \quad (2)$$

where a is a temperature independent empirical constant, $b = \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r \cdot C_0}{k_D + k_r}$, and

$c = ((k_D + k_r)/\phi)$, with $\Delta^c H_T^0$ - the standard combustion enthalpy, S - the exposed wire surface, k_D and k_r - the rate constants for diffusion and surface reaction, respectively, C_0 - the gas phase concentration of fuel and ϕ - a characteristic length which ensures the dimensional homogeneity of

$$\frac{dQ_r}{dt} = a + \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r \cdot C_0}{k_D + k_r} \approx a + \Delta^c H_T^0 \cdot S \cdot k_D \cdot C_0 \quad (4)$$

the last term corresponding to a diffusion controlled process. In this case the Arrhenius type regression:

$$d \ln(dQ_r/dt)/d(1/T) = -E_{a,D}/R \quad (5)$$

gives the activation energy of diffusion, $E_{a,D}$.

II. When $t \rightarrow 0$, then $((k_D + k_r)/\phi) \cdot t \ll 1$. If $t = \tau_s/z$, where $z > 1$ are integers or semi-integers, *i.e.* $z = 1.5, 2, \dots, 9 \dots$, (see Fig. 2) one obtains, for sufficiently large z , when the product

exponent ct . For a diffusion controlled process, when $k_r \gg k_D$, the limiting values of b and c are: $b^* = \Delta^c H_T^0 \cdot S \cdot k_D \cdot C_0$ and $c^* = k_r/\phi$, respectively.¹²

The reaction heat flow rate is directly proportional to the overall reaction rate, r_R :

$$dQ_r/dt = \Delta^c H_T^0 \cdot S \cdot r_R \quad (3)$$

and can be used as a measure of the reaction rate.

There are two limiting cases of equation (2):

I. When $t \rightarrow \tau_s$, then

$\exp(-((k_D + k_r)/\phi) \cdot t) \rightarrow 0$ and consequently:

$((k_D + k_r)/\phi) \cdot \tau_s/z \ll 1$ and the exponential can be approximated with $1 - ((k_D + k_r)/\phi) \cdot \tau_s/z$:

$$\left(\frac{dQ_r}{dt}\right)_z = a + \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r \cdot C_0 \cdot \tau_s}{\phi \cdot z} \quad (6)$$

The Arrhenius type regression gives in this limiting case:

$$d \ln(dQ_r/dt)_z/d(1/T) = -(E_{a,D} + E_{a,r})/R \quad (7)$$

if $\tau_s/z \approx \text{const}$ and z is sufficiently large.

From $t \rightarrow 0$, at the beginning of the ignition, up to $t \rightarrow \tau_s$, the activation energy should vary from overall diffusion plus surface reaction value, $(E_{a,D} + E_{a,r})$ diffusion value, $E_{a,D}$ from overall diffusion plus surface reaction value, $(E_{a,D} + E_{a,r})$ to diffusion value, $E_{a,D}$. The analysis of the short transient period, lasting from

several milliseconds up to several seconds, indicates the way the activation energy changes during the catalytic ignition process.

Equation (2) indicates also that the reaction heat flow rate is directly proportional to the fuel pressure, $C_0 = p_F/(RT)$, suggesting a first order with respect to the fuel, in agreement with the reported values. However it cannot predict the overall reaction order which also includes the partial reaction order with respect to oxygen.

RESULTS AND DISCUSSION

A typical plot $\ln(dQ_r/dt)_z$ versus $1/T$ is given in Fig. 3.

It can be observed that the slope increases for higher z . The regression analysis of these data led to the results shown in Table 1. The observed trend is in good agreement with the prediction of equations (4) and (6). For $t \rightarrow 0$, e.g. $t = \tau_s/9$, the activation energy is significantly larger than

for $t \rightarrow \tau_s$, when the overall process tends to become diffusion controlled, with low activation energy. For extrapolation to $t = 0$ ($\tau_s/z = 0$), the following function gave the best results (intersection with E_a axis, very good coefficient of determination, very large $F_{\text{statistic}}$ and random distribution of residuals):

$$E_a = a_0 + a_1 \cdot \exp(-a_2 \cdot \tau_s/z) \quad (8)$$

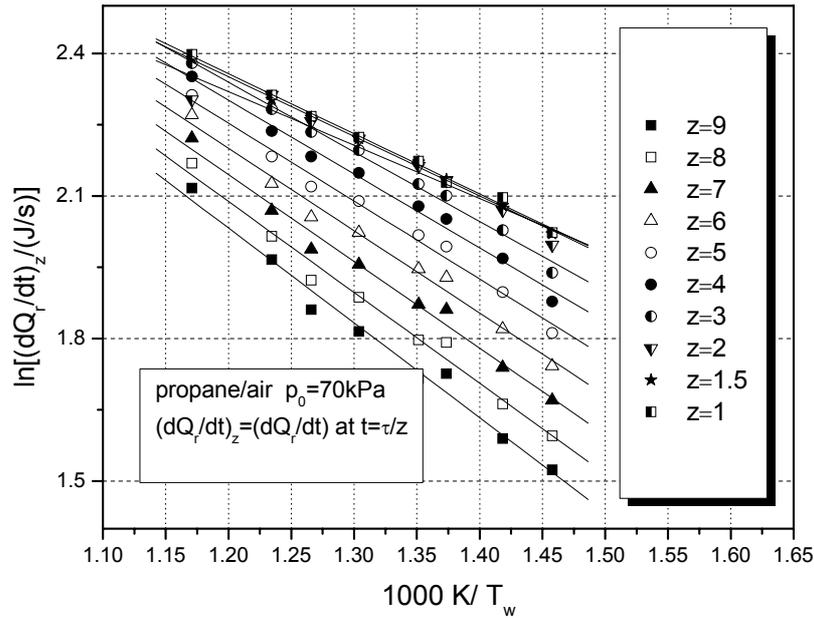


Fig. 3 – Arrhenius plots at different fractions of τ_s ($t = \tau_s/z$) for a stoichiometric propane/air mixture.

Table 1

Variation of activation energy (kJ/mol) during the transient period of ignition for stoichiometric propane/air mixture at several total pressures for $700 \text{ K} < T < 850 \text{ K}$

z	p_0/kPa			
	10	30	50	70
9	12.3 ± 0.8	10.0 ± 0.7	11.5 ± 0.7	16.6 ± 0.9
8	10.5 ± 1.2	9.6 ± 0.7	10.9 ± 0.7	15.9 ± 0.8
7	9.9 ± 1.3	9.2 ± 0.7	10.3 ± 0.7	15.2 ± 0.8
6	9.5 ± 1.1	8.9 ± 0.7	10.0 ± 0.7	14.4 ± 0.7
5	8.5 ± 0.1	8.8 ± 0.7	9.6 ± 0.5	13.6 ± 0.6
4	7.8 ± 0.6	8.7 ± 0.6	9.4 ± 0.5	12.9 ± 0.5
3	7.2 ± 0.3	8.8 ± 0.6	9.2 ± 0.8	12.2 ± 0.4
2	6.7 ± 0.2	8.7 ± 0.7	8.9 ± 0.9	9.4 ± 0.2
1.5	6.2 ± 0.6	8.6 ± 0.6	8.8 ± 1.1	10.4 ± 0.2
1	5.5 ± 0.6	8.7 ± 0.7	9.2 ± 1.1	10.5 ± 0.3

It should be emphasized that at high temperatures the activation energy of the surface reaction is generally much lower than that for the lower temperature range characteristic to catalytic ignition. This pattern was reported in different ways by many researchers in the field and confirms also the continuous decrease of the catalytic combustion reaction when the temperature increases. It is usually identified through a continuous slope change (decrease) of the Arrhenius type plots.¹⁴

A significant increase of the activation energy with the total pressure for $z = 1$ (diffusion controlled regime) can be observed, while for

different fractions of τ_s , the variations seem to be of no definite trend within the limits of experimental errors. It should be emphasized that the reaction heat flow rates for $z = 1$ (corresponding to the steady state reaction) can be measured with higher precision than those corresponding to $z > 1$, affected by larger errors induced by localization of τ_s .

The increase of the activation energy could be explained on the basis of a mechanistic Langmuir-Hinshelwood equation for a competitive, nondissociative adsorption of both reactants, without diffusion limitation:

$$r_R = k_R \cdot \frac{K_{ad,F} \cdot K_{ad,ox} \cdot p_F \cdot p_{ox}}{(1 + K_{ad,F} \cdot p_F + K_{ad,ox} \cdot p_{ox})^2} \quad (9)$$

where k_R is the rate constant of the surface reaction, $K_{ad,F}$, $K_{ad,ox}$ and p_F , p_{ox} are the adsorption-desorption equilibrium constants and

partial pressures of fuel and oxygen, respectively.^{3,12} The apparent activation energy, calculated as:

$$E_{ap} = -R \left(\frac{\partial \ln r_R}{\partial (1/T)} \right)_{p_j} = E_R + \Delta H_{ad,F} + \Delta H_{ad,ox} - \frac{2 \cdot \sum (K_{ad,j} \cdot p_j \cdot \Delta H_{ad,j})}{1 + \sum (K_{ad,j} \cdot p_j)} \quad (10)$$

where ΔH_{ad} are the adsorption enthalpies, takes the following form, which shows explicitly the

dependence on the total pressure, p_0 :

$$E_{ap} = E_R + \Delta H_{ad,F} + \Delta H_{ad,ox} - \frac{2 \cdot p_0 \cdot \sum (K_{ad,j} \cdot X_j \cdot \Delta H_{ad,j})}{1 + p_0 \cdot \sum (K_{ad,j} \cdot X_j)} \quad (11)$$

where X_j are the molar fractions of the components. Since $\Delta H_{ad} < 0$, adsorption being generally an exothermic process, the last term in equation (11) predicts an increase of the apparent activation energy at constant composition, when the total pressure increases, especially if $p_0 \cdot \sum (K_{ad,j} \cdot X_j) \ll 1$. At the other extreme, the

apparent activation energy becomes pressure independent.

Similar data were obtained for *n*-butane and *i*-butane. The conclusive results are summarized in Table 2, together with the reaction heat flow rates at $p_0=70$ kPa and $T=690$ K.

Table 2

Variation of activation energy during the transient period at $p_0=70$ kPa for C_3 and C_4 alkanes and of reaction heat flow rate

Fuel	E_a /(kJ/mol)			dQ_r/dt /(J/s)
	For $t \geq \tau_s$	For $t = \tau_s/9$	Extrapolated to $t = 0$	$p_0=70$ kPa $T=690$ K
propane	10.5	16.6	22.7	7.56
n-butane	9.3	18.6	29.1	8.05
i-butane	8.0	22.3	39.3	7.03

For the steady-state region, ($t \geq \tau_s$), the activation energy is characteristic to diffusion controlled processes, but increases within the transient period reaching the highest values at $t=0$. This composite activation energy does not follow the reported decreasing order of bond energy for their weakest C-H bond.⁴ It is also apparent that the reaction rate (proportional to dQ_r/dt) does not follow the trend suggested by the composite activation energy. Taking into account the complex

significance of the measured composite activation energy and its dependence on the operational parameters and on the selected model¹⁵, the obtained results bring additional viewpoints regarding the activation energy of the catalytic ignition, a subject abounding in scattered and contradictory data. Several results, reported in the pertinent literature for lower temperatures, including propane and butanes, are relevant for this subject as can be seen in Table 3.

Table 3

Reported activation energies (kJ/mol) and approximate temperature range (K) for catalytic ignition of alkane/air mixtures on platinum

Alkane	Ref. 16	Ref. 14	Ref. 4
C ₃ H ₈	92 (500-573)	97 (500-870)	80 (440-570)
<i>n</i> -C ₄ H ₁₀	105 (450-520)	71 (500-670)	-
<i>i</i> -C ₄ H ₁₀	-	56 (500-670)	80 (440-570)

It can be seen that the trend of our results agrees well with some reported data but disagrees with others. The lower values of the composite activation energies evaluated from our measurements as compared with those given in Table 3 are assignable to the different temperature ranges: lower temperatures for data in Table 3 and higher temperatures (700 – 850K) for our measurements as well as for short contact time reactors¹⁷, in agreement with the prediction resulted from Fig. 1.

CONCLUSIONS

The analysis of the measured reaction heat flow rate during the ignition process of stoichiometric propane or butanes/air mixtures, on isothermally heated platinum wires at various pressures and temperatures higher than the catalytic ignition temperatures, demonstrates the existence of a smooth transition between kinetic and diffusion control. This transition occurs within a short time interval, up to several seconds, dependent on the operational conditions, and can be rationalized using a simple kinetic model. It is characterized by a continuous decrease of the activation energy between two limiting values: a composite activation energy containing both diffusion and kinetic contribution and a diffusion activation energy reached during the steady-state combustion regime. For the chosen temperature range (700 – 850K), frequently used for short contact time reactors the composite activation energies, characteristic for the beginning of the ignition process, are lower than the activation energies reported in literature for combustion at lower temperatures or from measurements of ignition

temperatures. The trend of their variation with respect to alkane structure agrees well with some reported data but disagrees with others.

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